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VOLUME 8

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EDITORIAL NOTE

It is regretted that Professor N. F. Mott has decided to vacate the position of Editor of *Advances in Physics* owing to the pressure of other duties. However, he retains his interest in the journal, of which he was the first editor, by remaining as Consultant Editor. The publishers, and all concerned with *Advances in Physics*, extend to Professor Mott their grateful appreciation of all the work he has done for the journal.

ADVANCES IN PHYSICS

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PHILOSOPHICAL MAGAZINE

VOLUME 8

JULY 1959

NUMBER 31

Classical Theory of the Equilibrium Liquid Pair Distribution

By G. H. A. COLE

Physics Division, Clarke, Chapman & Co., Ltd., Gateshead, 8, Durham

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§ 1. INTRODUCTION

It is now customary to distinguish between the three main states of matter in terms of the ordering of the constituent molecules in space. In broad terms a crystalline solid is characterized by long-ranged ordering, in which a basic lattice arrangement is repeated in all directions from each point over distances large on a macroscopic scale: a dilute gas is, in contrast, characterized microscopically by complete spatial disorder. A simple liquid, thermodynamically and mechanically mid-way (in a certain sense) between these two extremes, is characterized by only short-ranged molecular spatial

ordering in which a definite and quite distinctive spatial arrangement is discernible in the immediate vicinity of each liquid molecule, but beyond this ordering breaks down completely. Intermediate states of matter are in broad terms represented by relaxing these idealized conceptions in appropriate ways.

In order to understand the properties of gross matter in terms of molecular properties (which may be taken to be the present aim of the kinetic theory) it is necessary to express these details of molecular spatial ordering in more precise and mathematical terms. For this purpose probability distribution functions have been defined so as to give the probability for the occurrence of a chosen number of molecules from a system of interest in a given configuration, within certain prescribed limits of accuracy. The most elementary distribution function is the singlet distribution which defines the probability for finding a chosen particle in any specified elementary configurational volume. It is this distribution that has found wide use in the theory of the dilute gas (Chapman and Cowling 1952). Complete information concerning the spatial arrangement in the system must involve a knowledge of the full hierarchy of distribution functions, i.e. in addition to the singlet distribution also the pair, triplet, quadruplet distributions, and so on, which describe the probability for finding respectively, two, three, four, five, and so on, chosen molecules in a given relative configuration. For liquids the pair distribution has so far played a very prominent rôle in the theory (see e.g. Cole 1956), for reasons which will be explained later.

The theory of liquid structure and properties has so far remained less developed than the corresponding theories of the dilute gas, and the crystalline solid, due to mathematical complexity. The special features of the spatial ordering for solids, viz. respectively long-ranged ordering with harmonic forces, and complete disorder, allow for important simplifications to be introduced into the associated mathematics in the treatment of these two states of matter. The short-ranged ordering characteristic of liquids does not permit of any corresponding reduction of the associated theoretical discussion, with the result that there is no alternative but to base the theory on a full N -body model. Any mathematical reductions that may be necessary for technical reasons must accordingly be in the nature of purely mathematical approximations. This must dictate the development of the theory since the effect of the approximations is to be made as small as is possible.

The present paper is concerned primarily with the theoretical determination of the pair distribution for a simple classical liquid under conditions of equilibrium. The discussion considers only arguments based strictly on the principles of particle dynamics and classical statistical mechanics, and does not appeal to special simplifications such as those used, for example, in the cell model: nor will the work of Meyer and Sarolla (1956) (see also Sarolla 1958) involving classes of integral equations be considered. The standard equations of statistical mechanics have been found in the past, even with approximations, to lead to significant results for simple liquids, and we will be concerned here with the extension and possible refinement

of these already partially tested methods. Conditions in the regions of a liquid boundary with another phase will not be considered.

After a brief statement of preliminary notions in § 2, the empirical determination of the radial distribution is considered in § 3. Then the general distribution functions are defined and investigated in § 4, the pair distribution itself being also isolated. In § 5 application to simple liquids is begun, according to that approach which involves the superposition approximation. The approximation itself is first stated, and some causes of error when it is applied to liquids are then isolated. The approximation of superposition is inserted into the theory in § 6, first through a first-order integro-differential equation, and then alternatively using a second-order equation. Because of the inadequate theoretical basis of the superposition approximation as usually stated, any full kinetic theory of liquids must include a procedure allowing for its effect to be continually minimized (ideally removed altogether), and this problem is formally investigated in § 7. In order to bring the discussion to a close the well-established relation between the pair distribution and liquid macroscopic thermodynamics is summarized for completeness in § 8, and the paper finishes with some brief conclusions (§ 9).

§ 2. PRELIMINARY NOTIONS

For the purposes of the theory, the simple liquid is represented by N identical particles, interacting one with another according to a definite law, and contained in a fixed volume V which may be very large. The details of the particles, such as mass and shape, are regarded as known, together with the law of force with which one particle acts upon another. No essential liquid properties are lost if internal particle degrees of freedom are neglected, provided that any associated external effects are included in the specification of the law of interparticle force. The broad features of this force are an extreme repulsion at small interparticle distances (representing molecular impenetrability and uniqueness), and an attraction at larger distances (accounting for macroscopic cohesion). For the simplest case of spherically symmetric particles the attractive force decreases with distance like r^{-7} : for more complex polar molecules it decreases more nearly like r^{-4} .

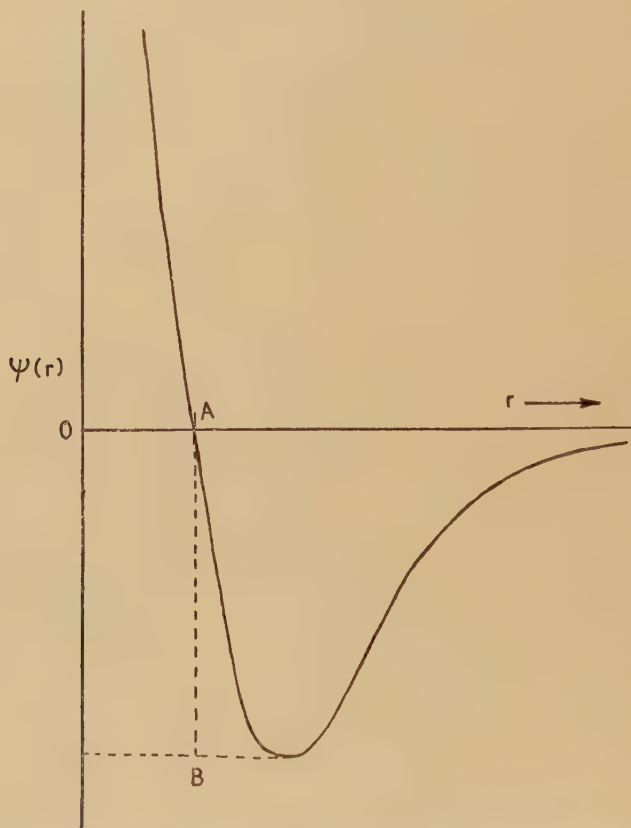
In fig. 1 is shown a curve, typical for non-polar spherical particles, for the dependence of the potential of the force (the negative force itself is derived by one differentiation with respect to the distance) upon the distance from its centre. Curves of this type are adequately represented by the expression (Mie 1903):

$$\psi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^m - \left(\frac{\sigma}{r} \right)^n \right] \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

where m and n are positive numbers. Here ϵ has the dimensions of energy and is given by the distance AB in fig. 1: σ has the dimensions of a length and is equal to the distance OA in fig. 1. σ can be interpreted physically as the classical particle radius, whereas ϵ is the maximum negative value of

the potential ψ . Lennard-Jones (1937) has shown that the special case of eqn. (2.1) with $m=12$ and $n=6$ applies well to many substances. For the classical liquid argon, Rushbrooke (1940) finds $m=11.4$ is even more accurate than $m=12$ in (2.1) and quotes the relations $4\epsilon\sigma^{11.4}=3.62 \times 10^{-8}$ and $4\epsilon\sigma^6=1.11 \times 10^{-10}$ (ϵ in ergs and σ in ångström units). With these values of the parameters in (2.1) it is found that $\psi(r)$, and so also the interparticle force, becomes negligibly small at a distance of about three molecular diameters (i.e. $r \sim 6\sigma$): for dipolar molecules this distance is somewhat greater.

Fig. 1



Curve for the dependence of the interparticle potential of the force, $\psi(r)$, on the distance, r , for a typical non-polar liquid.

The three main states of matter (solid, liquid, and gas) form for any given substance a hierarchy of energy content, the solid containing least, and the gas most, energy: this is very elementary knowledge. It is also elementary knowledge that matter expands on heating, only by some 4% across the (essentially discontinuous) melting region but greatly across the condensation region, all cohesion being lost. Because the molecular size can for our present purposes be taken to be temperature independent, the volume

variants consequent upon temperature change must be ascribed to molecular relative configurational rearrangements. The expression $(3V/4\pi N)^{1/3}$ has the dimensions of a length and may be loosely interpreted as the mean distance between constituent particles in a given specimen. By using considerations of this type it has generally been inferred that the mean distance between the centres of molecules in a solid is of the order of 1.2 molecular diameters; for a liquid it is slightly greater, being about 1.4 diameters; but for a gas under normal pressure it is certainly greater than 10 diameters.

These simple considerations lead, in combination with eqn. (2.1), to far reaching conclusions. For the mean molecular separation in both solids and liquids is less than the effective range of the interparticle force, whereas it is far greater than this range for a gas. For a solid or a liquid, therefore, the constituent molecules are continuously in the force field of neighbours, whereas in a gas they almost never are. Binary molecular collisions, which play so important a rôle in a gas, are virtually unknown in condensed matter: more particularly any transfer of energy or momentum in condensed matter occurs through the action of the interparticle force in contrast to the corresponding mechanism in a dilute gas which depends upon direct particle collisions.

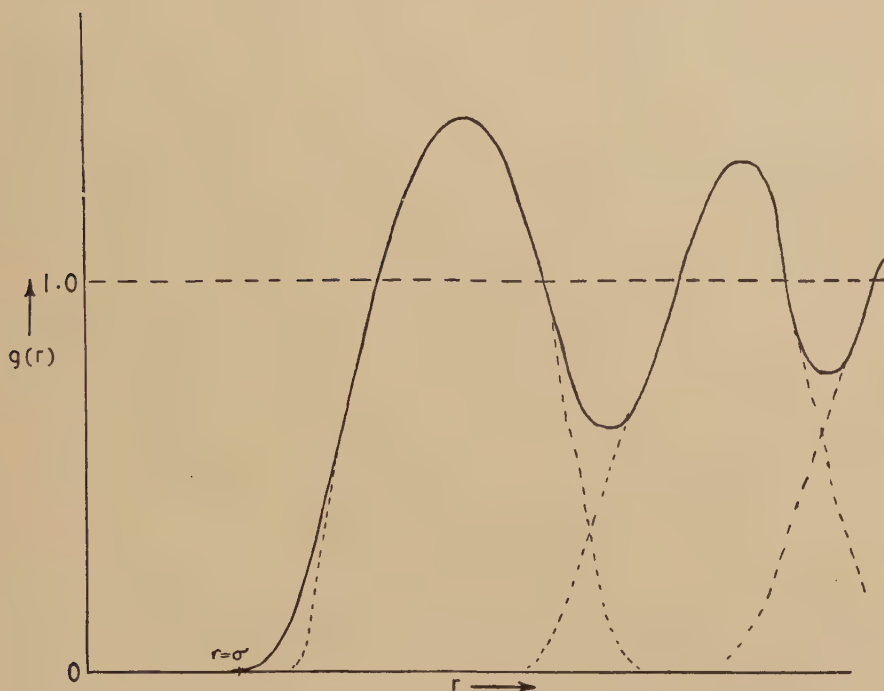
Any interparticle force law of physical interest must ascribe a greater effect on the motion of any chosen particle to near neighbours than that due to more distant neighbours. To make the mathematical analysis more tractable it is further sufficient to assume for many physical systems that the action of a number of particles on a chosen particle is the simple sum of the effect of each particle separately in the absence of the remainder. This reduction expressed alternatively postulates that only the mutual interaction between particle pairs is significant, all other interactions being negligible. The distribution of pairs of particles in the volume is consequently of prime interest: this situation seems to hold to sufficient approximation in simple liquids. The short-ranged molecular spatial ordering characteristic of a liquid, which requires definite configurational ordering for only some twenty particles lying in a volume of three or four particle diameters around any chosen particle as centre, can involve only the lower-order distribution functions. In particular it can be hoped that the more obvious liquid properties can be understood by an appeal to the distribution of particle pairs alone. As the particle kinetic energy decreases, and the solid state is reached, the effect of the interparticle force is enhanced and the pair distribution tends to lose its pre-eminence in the theory. The deduced importance of the pair distribution in the theory of liquids is plausible, but must now be investigated more carefully.

§ 3. THE RADIAL DISTRIBUTION

The molecular spatial ordering in matter has been determined experimentally by the diffraction of electromagnetic radiation, principally x-rays (Gingrich 1943), and alternatively neutrons have been used for this

Two comments concerning (3.3) are relevant here. The first is that all small angle scattering is neglected in accord with the previously agreed neglect of particle internal degrees of freedom. The second comment is that the theory provides directly $I(s)$ as function of a distance integral containing $g(r)$: the form (3.3) is then obtained by carrying through a Fourier inversion. Some consequent error is in this way introduced into the fine details of $g(r)$ although the broad features are reliable. The point to notice is that the details of $g(r)$ determined from (3.3) are subject to some small error which cannot easily be exactly ascertained.

Fig. 2



Typical radial distribution for a simple liquid. The x-ray intensity pattern from which such a curve is derived shows a strong resemblance to, though non-identity with, the pattern obtained by using a fine powder of crystallites.

The application of eqn. (3.3) to the study of fluids shows results that mirror the effects of both classical molecular radius, σ , and the effect of the interparticle force in liquids. For a dilute gas it is found that $g(r)$ is zero for $r < \sigma$ (particle impenetrability), and is unity for all other values of the separation distance between a pair of molecules. For a liquid it is again found that $g(r)$ vanishes for $r < \sigma$, but for $r > \sigma$ the radial distribution has a fluctuating form about the value unity. As the separation distance becomes greater the fluctuations become rapidly smaller, vanishing in the

configuration volume $d\mathbf{r}_1$ about the configuration point \mathbf{r}_1 , and simultaneously particle 2 in the elementary volume $d\mathbf{r}_2$ about \mathbf{r}_2 , and simultaneously the i th particle in the elementary volume $d\mathbf{r}_i$ about \mathbf{r}_i ($i = 3, 4, 5, \dots N$) will be written

$$n^N n^{(N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N \quad . \quad . \quad . \quad (4.1)$$

where $n = N/V$: in the usual experimental nomenclature of § 3 it is seen that $n \equiv \rho_0$. Because n^N has the dimensions of V^{-N} it follows that $n^{(N)}$ defined in (4.1) is dimensionless.

For sub-systems, the probability for finding h ($< N$) chosen particles in the elementary configuration volume $(d\mathbf{r}_1, d\mathbf{r}_2, d\mathbf{r}_3, \dots d\mathbf{r}_N)$ centred about the configuration point $(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_N)$ will be written

$$n^h n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_h \quad (h = 1, 2, 3, \dots). \quad (4.2)$$

The dimensionless probability functions $n^{(N)}$ and $n^{(h)}$ will be called the distribution functions of order N and h respectively. The various distribution functions can be related either according to any order, or for consecutive orders. In the first case $n^{(h)}$ (if $h < N$) is derivable from $n^{(N)}$ by averaging over the partial configuration of the unwanted particles. Expressed alternatively, for a system of identical particles,

$$n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h) = \frac{N!}{(N-h)!} n^{(N-h)} \int \dots \int n^{(N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_N) d\mathbf{r}_{h+1} \dots d\mathbf{r}_N. \quad . \quad . \quad . \quad (4.3)$$

This applies for any order h . A simple corollary shows the consecutive distribution functions $n^{(h)}$ and $n^{(h+1)}$ to be related according to

$$n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h) = \frac{n}{(N-h)} \int n^{(h+1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h, \mathbf{r}_{h+1}) d\mathbf{r}_{h+1}. \quad (4.4)$$

The definitive relations apply at each time instant, but because only uniform situations are considered here, it is unnecessary to mention the time explicitly in the formulae.

In order that the expressions (4.1) to (4.4) shall have value in connection with actual systems it is necessary to make appeal to physical arguments for defining one distribution function in terms of physically measurable quantities. When one such function is known the remaining $(N-1)$ functions are formally defined and can, in principle at least, be explicitly derived. In practice, however, severe difficulties are found in carrying through such a derivation for a general system of particles.

Following Gibbs it is usual to choose the N th order distribution as the one to be defined. For this purpose the canonical form is invoked (Tolman 1938):

$$n^{(N)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_N) = \frac{1}{N! Z} \exp\{-X(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_N)\} \quad . \quad (4.5)$$

where Z is the configurational partition function defined to normalize $n^{(N)}$ to unity, i.e.

$$Z = \frac{1}{N!} \int \dots \int \exp\{-X\} d\mathbf{r}_1, d\mathbf{r}_2, d\mathbf{r}_3, \dots d\mathbf{r}_N. \quad . \quad . \quad (4.6)$$

In (4.5) and (4.6), X is the dimensionless reduced total potential energy of the system, related to the actual total potential energy Ψ according to

$$kT X(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N). \quad (4.7)$$

The reasons for choosing the form (4.5) need not be rehearsed here, beyond the statement that this expression is in accord with the macroscopic thermodynamic features of the associated physical uniform system. (For full discussion, see Tolman's book, referred to above.)

For simple systems it was seen in § 2 that the total interaction can be adequately represented by the sum of the separate mutual pair interactions, and this will be assumed true in what follows. A reduced pair interaction potential, $\chi(\mathbf{r}_i, \mathbf{r}_j)$, is therefore defined according to

$$kT \chi(\mathbf{r}_i, \mathbf{r}_j) = \psi(\mathbf{r}_i, \mathbf{r}_j) \quad (4.8)$$

to describe the interaction between particles i and j . If $\mathbf{r}_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, then for the case of particle spherical symmetry \mathbf{r}_{ij} is angular independent, becoming simply the interparticle distance r : in this case $\psi(\mathbf{r}_i, \mathbf{r}_j)$ is to be written as $\psi(r)$ and has the form described by (2.1) and shown in fig. 1. The total potential X is related to χ :

$$X(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) = \sum_{i=1}^N \sum_{j>i}^N \chi(\mathbf{r}_i, \mathbf{r}_j); \quad (4.9)$$

i.e. X is equated to the sum of $\frac{1}{2}N(N-1)$ binary terms.

In describing the microscopic configuration of a simple liquid at macroscopic temperature T the formulae (4.1) to (4.4) will be invoked together with the expressions (4.5) and (4.9).

4.1. Dependence on Small Configuration Changes

Small changes of the relative particle configuration affect the distribution functions in a way that can be calculated by an appropriate differentiation of the distribution functions defined above. Since such changes will be of interest in § 6 it is convenient to collect the several expressions here.

Suppose one particle of the group of h forming a sub-system, say particle i , ($1 \leq i \leq h$), moves its position by an infinitesimal amount, $\Delta \mathbf{r}_i$. Although formally the separate values of the distribution function $n^{(h)}$ corresponding to the two particle configurations $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i, \dots, \mathbf{r}_h)$ and $(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_i + \Delta \mathbf{r}_i, \dots, \mathbf{r}_h)$ are linked through the formula of the Taylor expansion, in practice this approach is of no interest for very obvious mathematical reasons. In particular it is necessary to know the details of the distribution functions $n^{(h+m)}$ where $m = 1, 2, 3, \dots$, in addition to the configuration derivatives $\partial^m n^{(h)} / \partial \mathbf{r}_i^m$.

The first two derivatives are, however, of interest in themselves, since the first derivative describes the gradient of $n^{(h)}$ at the configuration point in question, while the second derivative is a measure of the deviation of the

distribution function at the point from the local mean value. Using eqn. (4.3) together with the expressions (4.5) and (4.8) it follows that the partial gradient of $n^{(h)}$ is given by

$$\frac{\partial n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h)}{\partial \mathbf{r}_i} = - \sum_{\substack{j=1 \\ \neq i}}^h \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_j)}{\partial \mathbf{r}_i} n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h) \\ - n \int \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_{h+1})}{\partial \mathbf{r}_i} n^{(h+1)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots \mathbf{r}_h, \mathbf{r}_{h+1}) d\mathbf{r}_{h+1} \dots \dots (4.10)$$

It is seen that the calculation of the gradient of $n^{(h)}$ at any configuration point involves a knowledge of $n^{(h)}$ and $n^{(h+1)}$ at that point.

The second derivative of $n^{(h)}$ with respect to \mathbf{r}_i follows by differentiating (4.3) twice and using (4.4) with h replaced by $(h+1)$. Carrying through this procedure :

$$\frac{\partial^2 n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_h)}{\partial \mathbf{r}_i^2} = - \sum_{j=1}^h \left[\frac{\partial^2 \chi(\mathbf{r}_i, \mathbf{r}_j)}{\partial \mathbf{r}_i^2} - \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_j)}{\partial \mathbf{r}_i} \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_j)}{\partial \mathbf{r}_i} \right] \frac{\partial n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_h)}{\partial \mathbf{r}_i} \\ - n \int \left[\frac{\partial^2 \chi(\mathbf{r}_i, \mathbf{r}_{h+1})}{\partial \mathbf{r}_i^2} + \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_{h+1})}{\partial \mathbf{r}_i} \frac{\chi(\mathbf{r}_i, \mathbf{r}_{h+1})}{\partial \mathbf{r}_i} \right] \\ \times n^{(h+1)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_{h+1}) d\mathbf{r}_{h+1} \\ - n^2 \int \int \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_{h+1})}{\partial \mathbf{r}_i} \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_{h+2})}{\partial \mathbf{r}_i} \\ \times n^{(h+2)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_{h+1}, \mathbf{r}_{h+2}) d\mathbf{r}_{h+1} d\mathbf{r}_{h+2} \dots \dots (4.11)$$

This expression involves a knowledge of $n^{(h+2)}$ in addition to a knowledge of $n^{(h)}$ and $n^{(h+1)}$.

4.2. Dependence on Temperature Change

The potential energy function Ψ is temperature independent to very good approximation: in consequence the reduced potential X is affected by temperature change only through the factor T^{-1} . The distribution functions therefore depend upon the temperature in a simple manner which may be determined by the direct temperature differentiation of equation (4.3) using (4.5) and (4.9). For an indefinitely small temperature increment ΔT , the consequent change in $n^{(h)}$ is :

$$\frac{\partial n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_h)}{\partial T} \Delta T = \left\{ n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_h) \left[\sum_{i=1}^h \sum_{j>i}^{(h-1)} \chi(\mathbf{r}_i, \mathbf{r}_j) + \mathcal{A} \right] \right. \\ + n \int \left(\sum_{i=1}^h \chi(\mathbf{r}_i, \mathbf{r}_{h+1}) \right) n^{(h+1)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_h, \mathbf{r}_{h+1}) d\mathbf{r}_{h+1} \\ + n^2 \int \int \chi(\mathbf{r}_{h+1}, \mathbf{r}_{h+2}) n^{(h+2)}(\mathbf{r}_1, \mathbf{r}_2, \dots \mathbf{r}_{h+1}, \mathbf{r}_{h+2}) \\ \left. \times d\mathbf{r}_{h+1} d\mathbf{r}_{h+2} \right\} \Delta T. \dots \dots (4.12)$$

In this expression the quantity \mathcal{A} is defined as being :

$$\mathcal{A} = \frac{1}{T} \int \int \chi(\mathbf{r}_1, \mathbf{r}_2) n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{TV^{(h-2)}} \int \dots \int \chi(\mathbf{r}_1, \mathbf{r}_2) n^{(h)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_h) \times d\mathbf{r}_1 d\mathbf{r}_2, \dots d\mathbf{r}_h. \quad (4.13)$$

The bracket expression on the right-hand side of eqn. (4.12) applies to the temperature T : it is seen to involve a complete knowledge at this temperature of the distribution functions $n^{(h)}$, $n^{(h+1)}$, and $n^{(h+2)}$.

Higher derivatives of temperature than the first need not be considered if ΔT is sufficiently small : any extended increment can be built up from a suitable number of elementary elements.

4.3. Pair Distribution

The liquid short-ranged order is to be represented, according to § 3, in the general case by the pair distribution, $n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$, which gives the probability for the occurrence of a pair of particles in the system at any given vector separation. In application to liquids, therefore, the formulae developed in this section are to be arranged so that $h=2$. It follows that several lower order distribution functions are also involved in addition to $n^{(2)}$, viz. $n^{(3)}$, and $n^{(4)}$ at least.

The pair distribution itself is defined by eqns. (4.3) and (4.5) with h set equal to 2, and for simple liquids (4.9) is to be added as a supplement. Some knowledge of $n^{(2)}$ is axiomatically available for three special limiting (boundary) conditions : for vanishing pair particle separation at constant temperature the pair distribution must vanish in conformity with particle impenetrability ; for indefinitely large pair separations at constant temperature the two particles are essentially independent (liquid short-ranged order) ; and in the limit of indefinitely high temperatures (dilute vapour) the particles are essentially independent. These three boundary conditions can be summarized in the form

$$\left. \begin{array}{ll} (a) & n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0 \quad (|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow 0), \\ (b) & n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 1 \quad (|\mathbf{r}_1 - \mathbf{r}_2| \rightarrow \infty), \\ (c) & n^{(2)}(T) \rightarrow 1 \quad (T \rightarrow \infty). \end{array} \right\} \quad \dots \quad (4.14)$$

Any calculation of the pair distribution must provide data satisfying these three conditions. In conclusion it will be realized that in the special case of interparticle central force fields the pair distribution $n^{(2)}$ becomes identical with the experimental radial distribution $g(r)$ introduced in § 3.

§ 5. SUPERPOSITION APPROXIMATION

It is well known that any direct evaluation of the integral appearing in the partition function, defined in (4.6), for models of physical interest in connection with condensed matter (where $n \sim 10^{25}$ particles per unit volume) is quite impractical whatever the available computational facilities. The same holds true for the direct evaluation of the expression for the pair

distribution, viz. (4.5) and (4.9) inserted into (4.3) with $h=2$, since this is essentially an identical problem to the evaluation of Z ; this is also true for the further cases $h=3, 4$, and 5 . The several formulae involving the distribution functions, and considered in the last section, can therefore be used in practice only if relations are known which allow the functions $n^{(h+1)}$, $n^{(h+2)}$, and so on, to be expressed explicitly in terms of the single distribution $n^{(h)}$.

For liquids depending on pair forces (i.e. for which (4.9) is valid) it is the triplet and quadruplet functions $n^{(3)}$ and $n^{(4)}$, and possibly also the quintuplet function $n^{(5)}$, that must be known, preferably explicitly in terms of $n^{(2)}$.

This closure of the equations as they stand cannot be extracted from the theory at the present time, and it is necessary to introduce an approximation into the arguments at this point which, so far, have been a rigorous development of the well-established theory of classical statistical mechanics.

5.1. Statement of the Approximation

The requirement for the closure of the equations of the last section is that the correlation between a chosen group of h particles shall be replaced by the product of the correlations between the particles of the sub-groups that constitute the chosen group. Because the total interaction energy can be expressed in terms of the basic pair interaction, the approximation to be introduced into the theory, for reasons of mathematical convenience, can ultimately be stated in a form that represents the correlation between a large number of particles as the superposition of the correlations between the composing particle pairs. This superposition approximation, which is adequately valid in the theory of the dilute gas and in certain cases in the description of crystalline solids, was first applied to the discussion of liquids by Kirkwood (e.g. Kirkwood and Boggs 1942).

When applied to a particle triplet, $n^{(3)}$, the superposition approximation asserts the equality between the probability of a given triplet configuration and the product of the separate pair distributions:

$$n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) n^{(2)}(\mathbf{r}_1, \mathbf{r}_3) n^{(2)}(\mathbf{r}_2, \mathbf{r}_3). \quad (5.1)$$

For a particle quadruplet the corresponding reduction is the product of a given triplet configuration function and the pair functions formed by linking the remaining particle with the triplet constituents separately:

$$n^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) n^{(2)}(\mathbf{r}_1, \mathbf{r}_4) n^{(2)}(\mathbf{r}_2, \mathbf{r}_4) n^{(2)}(\mathbf{r}_3, \mathbf{r}_4). \quad (5.2)$$

For a particle quintuplet the form of the superposition approximation is clear:

$$n^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5) = n^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \left\{ \prod_{i=1}^4 n^{(2)}(\mathbf{r}_i, \mathbf{r}_5) \right\} \quad (5.3)$$

and so on for higher order distributions. It is immediately evident that a distribution of any order can, in this way, be reduced to the product of pair distributions. By invoking the superposition approximation each of the equations of § 4 can be arranged to contain the lowest order of distribution function initially present together with a number of pair distributions.

5.2. *Implications*

Before considering the introduction of the superposition approximation into the theory of liquids it is necessary first to make some investigation of the physical implications of its use.

The central approximation introduced by the superposition approximation in the form (5.1) to (5.3) is the independence of particles. Indeed these expressions become exact only in the limit when the energy of the interparticle force is negligible in comparison with the particle kinetic energy (i.e. when the reduced potential of particle interaction is essentially zero), and when the particle volume is negligibly small so that almost no elements of configuration volume are denied to each particle involved. Clearly the second of these conditions can never be exactly true in real matter although in the dilute gas it may be a good approximation to reality. Again the relative unimportance of the action of the interparticle force, as required by eqns. (5.1) to (5.3), is a very reasonable approximation for the dilute gas, but, remembering the conclusions of § 2, is really inadmissible in liquids.

The inadequacy of the superposition approximation for liquids when applied directly to the equations of § 4 is made immediately clear by the insertion of (5.1) into (4.4) with $h=2$. For it follows that $n^{(2)}$ must now satisfy the integral equation

$$\int n^{(2)}(\mathbf{r}_1, \mathbf{r}_3) n^{(2)}(\mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 = Nn^{-1} = \text{constant}.$$

The integral is, accordingly, independent of the positions of particles 1 and 2, and the corresponding pair interaction does not appear. Such a conclusion is not of physical interest so that the direct application of (5.1) to the equations of the theory of liquids is not permissible.

This does not mean that the superposition approximation cannot be applied to the theory of liquids. Rather it means that the theory must be appropriately moulded to receive it: explicitly the liquid structure is to be described by equations which minimize as far as possible the explicit effect of the interparticle force field. There remains the alternative approach of attempting to correct the superposition approximation, either using a definite mathematical procedure or by adding essentially *ad hoc* inferred correction terms. This alternative discussion would involve a careful assessment of the exact validity and scope of the superposition approximation, but so far no author seems to have attempted this. In the present discussion the approximation will be accepted as it stands, even though it lacks adequate theoretical backing, so that its usefulness in any particular form of the theory can be judged ultimately only in relation to the reliability of the predictions to which it leads.

§ 6. APPLICATION TO THE PAIR DISTRIBUTION

The problem to be considered now is the use of the superposition approximation, in the form exemplified in eqns. (5.1) to (5.3), to the equations of § 4 as they stand. In particular, concern now is only with the pair distribution which, it is reasonable to suppose in the light of § 3, is sufficient for a broad understanding of the structure of a simple liquid.

It was seen in the last section that the direct use of (5.1) in (4.4), with h set equal to 2, is not of physical consequence, so that a direct determination of $n^{(2)}$ itself cannot, by the present approach, be achieved. Information concerning $n^{(2)}$ can, however, be inferred alternatively from a knowledge of the first (gradient) or second space differentials of $n^{(2)}$. Provided that only indefinitely small changes of configuration are involved, the interparticle force can be expected to play only a secondary rôle in these changes. Both eqns. (4.10) and (4.11) have been quoted in this connection, and these expressions will now be considered separately.

6.1. First-order Equation

For the case $h = 2$, eqn. (4.10) involving the space gradient of $n^{(2)}$ can be written :

$$\frac{\partial n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} + \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -n \int_0^\infty \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_3)}{\partial \mathbf{r}_1} n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3. \quad (6.1)$$

This vector equation of the first order, derived independently by Yvon (1935) and Born and Green (1946), is strictly non-linear. It is to be solved so as to satisfy one of the boundary conditions (4.14*a*) or (4.14*b*). In order to derive $n^{(2)}$ it is necessary to know $n^{(3)}$ appearing under the integral sign on the right-hand side, and for this purpose, appeal is made to the approximation (5.1).

The simplest situation is that applying to a central force field; in this case the vector eqn. (6.1) with three components reduces to a scalar equation since now only one component (viz. that showing symmetry about the line joining the particle pair as axis) does not identically vanish. For such spherical symmetry the Born-Green-Yvon equation can be written in the scalar form :

$$\frac{\partial}{\partial r_{12}} \{ \log n^{(2)}(r_{12}) + \chi(r_{12}) \} = -n \int_0^\infty \frac{\partial \chi(r_{13})}{\partial r_{13}} n^{(2)}(r_{13}) n^{(2)}(r_{23}) 4\pi r_{13}^2 dr_{13} \quad (6.2)$$

where now $|\mathbf{r}_i - \mathbf{r}_j|$ is written simply as r_{ij} , $n^{(2)}(\mathbf{r}_i, \mathbf{r}_j)$ is written $n^{(2)}(r_{ij})$, and $\partial/\partial \mathbf{r}$ is replaced by $\partial/\partial r$. The solution procedure is still complex since the non-linearity of the equation remains for spherical symmetry.

Kirkwood and Boggs (1942) have also proposed a first-order equation different from (6.1) but apparently equivalent to it, using a coupling parameter. This equation will not, however, be written down here.

Analytic solutions of (6.2) have been attempted by Green (1947, 1952), Rodriguez (1948), and McLellan (1952): Scoins (1952) later criticized Green's solution. The analytic approach must, at the present time, involve a linearization of the equation if it is to be successful and tractable. This throws grave doubts on the validity of relating the derived solution to the measured properties of a physical liquid: in practice the analytic solutions have proved disappointing.

Important numerical solutions of (6.2) have been reported by Kirkwood and his school, using electronic computational techniques, for data adapted to liquid argon, this being treated as the typical monatomic (i.e. spherically symmetric) classical liquid whose molecular properties are known. First Kirkwood *et al.* (1950) considered the rather unrealistic case of a system of hard spheres (hard-core model), each spherical particle having a radius equal to the classical radius (σ) for argon. This model neglects the attractive interparticle force region altogether, and greatly strengthens the repulsive region. The calculated pair distribution, however, shows a surprising similarity to the measured data for liquid argon in spite of the restrictions of the molecular model. It must not immediately be concluded that the attractive forces play no essential rôle in determining the pair distribution. Although the hard core model takes no explicit account of the attractive force, it is implicitly present due to the mutual shielding of one particle of the pair by the other from the action of neighbouring particles. The attractive region of the inter-particle force field was explicitly accounted for approximately by Kirkwood *et al.* (1952) who added to the hard particle core model an attractive force outside the core having the appropriate form given by Lennard-Jones (1937) for argon. Equation (6.2) was first solved in the linear approximation, the non-linearities then being gradually accounted for by an iterative process. The data calculated in this way agree rather better with the experimental data than those obtained by the hard-core model; but the uncertain errors in the experimental data make such a comparison indecisive. It can, however, be concluded that the use of the superposition approximation, in the form (5.1), to a suitably modified form of the equations of statistical mechanics leads to significant information about the structure of a simple liquid.

Remembering the identity between $g(r)$ and $n^{(2)}$, a comparison between eqns. (6.1) in the form appropriate to central forces, and the earlier eqn. (3.7) gives some information concerning the average force on a particle. For it follows that the average force acting on a typical particle in the liquid can be expressed in terms of the pair and triplet distributions according to

$$\mathcal{F}(r_{12}) = -\frac{\partial\psi(r_{12})}{\partial r_{12}} - \frac{n}{n^{(2)}(r_{12})} \int_0^\infty \frac{\partial\psi(r_{13})}{\partial r_{13}} n^{(3)}(r_{12}, r_{13}, r_{23}) 4\pi r_{13}^2 dr_{13}.$$

It will be seen that the temperature does not explicitly appear in this expression, so that it is more natural for the actual potential to be used than the reduced potential. In the case of increasingly high dilution, the second term on the right hand side tends to vanish leaving the simple interaction between two particles. It is the second term involving the triplet function that distinguishes the force on a particle in a condensed system from that corresponding to an uncondensed system of particles.

6.2. Second-order Equation

While the superposition approximation was useless in connection with the zero-order integral eqn. (4.4), with h set equal to 2, its real value in connection with the scalar form of the first-order integro-differential eqn. (6.1) has

been demonstrated by Kirkwood and his school. It might be hoped, and can be expected, that the errors introduced into the theory will be reduced still further if the first-order equation derived from (4.10) is replaced by the second-order equation deduced from (4.11). With $h = 2$, this later equation can be written (Cole 1958 a):

$$\frac{\partial^2 n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1^2} + A(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial n^{(2)}(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} + B(\mathbf{r}_1, \mathbf{r}_2) n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = C(\mathbf{r}_1, \mathbf{r}_2) \quad (6.3)$$

where

$$A(\mathbf{r}_1, \mathbf{r}_2) = 2 \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} : B(\mathbf{r}_1, \mathbf{r}_2) = \left[\frac{\partial^2 \chi(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1^2} + \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} \cdot \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} \right] \quad (6.4a)$$

and further:

$$C(\mathbf{r}_1, \mathbf{r}_2) = -n \int \left[\frac{\partial^2 \chi(\mathbf{r}_1, \mathbf{r}_3)}{\partial \mathbf{r}_1^2} - \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_3)}{\partial \mathbf{r}_1} \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_3)}{\partial \mathbf{r}_1} \right] n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 \\ - n^2 \int \int \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_3)}{\partial \mathbf{r}_1} \frac{\partial \chi(\mathbf{r}_1, \mathbf{r}_4)}{\partial \mathbf{r}_1} n^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) d\mathbf{r}_3 d\mathbf{r}_4 \quad (6.4b)$$

This second-order integro-differential non-linear tensor equation is to be solved using both the boundary conditions (4.14a) and (4.14b). In its solution, the superposition approximation is to be applied in the forms (5.1) and (5.2). As for the vector eqn. (6.1) so also for the tensor eqn. (6.3), the only remaining component in the case of spherical particle symmetry is that component showing symmetry about the line joining the particles of the pair as axis.

While the direct solution of (6.3) even for particle spherical symmetry must be a very formidable task it has been suggested (Cole 1958a), though not tested by numerical calculation, that the equation may be of value in correcting approximate data for the pair distribution which may already be known (Cole 1958b). For this purpose the right-hand side of (6.3) is to be evaluated on the basis of the approximate pair distribution data using (5.1) and (5.2): more accurate data may then be determinable by applying an iterative procedure in which the right-hand side of (6.3) is one approximation lower than the left-hand side. The associated numerical work, although involving only elementary operations, is certain to be lengthy, and the use of electronic computational aids would almost certainly be necessary.

The approximate data might come from one of two sources. One is experimental, whereby diffraction data derived according to the arguments of § 3 can be corrected within the limits of the approximation of superposition. This procedure might be useful in gauging the reality of the details of the measured data for the pair distribution. For the special case of argon the data calculated by Kirkwood and his collaborators, using (6.1) and the modified hard-core model, might be corrected for an empirically correct interparticle force potential by using (6.3) together with the iterative procedure mentioned above. There would seem to be no convenient analytic method of testing the convergence of the iterative process, nor of showing that the solution of (6.3), which for a common potential function

differs from that of (6.1) only because of the differing use of the superposition approximation, is nearer to the measurable pair distribution than the solution of (6.1). The method has, however, the great advantage that the equation is linearized by the insertion of the approximate data for $n^{(2)}$ into the integral appearing on its right-hand side, so that (6.3) is to be regarded as a linear equation in such connections. It has the disadvantage that the superposition approximation must be applied to $n^{(4)}$ in addition to $n^{(3)}$.

Presumably there remains the possibility that the solution of (6.1), using an approximate potential function such as that of the modified hard core, could act as the first approximation in an iterative procedure using (6.1) itself, if for the correcting procedure the approximate potential is replaced by the empirically correct function. However, it can be expected that such a procedure would not lead to as accurate data for the pair distribution as that obtained from the equivalent procedure using (6.3).

These are matters of accuracy and detail: the results of the calculations of Kirkwood and his school suggest that significant information concerning the structure of simple uniform liquids can be obtained from the well-established principles of statistical mechanics even within the restrictions of the superposition approximation.

§ 7. RE-INTRODUCTION USING VARIABLE INTERPARTICLE COUPLING

The superposition approximation in the form (5.1) to (5.3) is dubious in its application to liquids, and any complete kinetic theory of simple liquids must treat very carefully the introduction of this approximation into the theory†. Ideally the need exists of avoiding its use altogether, but no-one has yet shown even formally how this may be achieved. In the absence of such a demonstration there are two broad directions that may be taken if the rôle of the approximation is to be minimized.

The first is the correction of the approximation according to a proper mathematical procedure, but this must be difficult since it is related to the problem of the abolition of the approximation itself. A correction based on *ad hoc* arguments, while theoretically unsatisfactory, would have some value, but no attempts at such a thing seem to have been reported. There is, also, the future possibility of deriving information about the triplet function using computational methods in connection with mathematical models (Wainwright and Alder, 1958, Wood *et al.* 1958). The technique, however, is not yet sufficiently developed in precision for this purpose.

The second approach is less theoretically ambitious. While accepting the need to invoke the superposition approximation, the aim now would be to avoid its use in $n^{(3)}$ (and possibly also in $n^{(4)}$ and $n^{(5)}$) by relating this function in a direct and tractable way to the distribution functions of higher order. The heavy numerical work that is bound to be associated with any application of this approach even to simple liquids might still not be unreasonable if $n^{(3)}$ only were freed directly from the approximation, but the

† It is for this reason that Mayer and Sarolla (1956) have considered the alternative possibility of using integral equations other than those employed in the previous section.

benefit to the theory would be great. One method of achieving this aim has recently been proposed by Cole (1959), using an argument based on a method involving a (hypothetical) variation of the interparticle coupling. It is, therefore, in the same spirit as some earlier work of Kirkwood and Boggs (1942).

7.1. Coupling Parameter

The solutions of the formulae set down in § 4 are controlled by the details of the reduced potential χ : in addition the physical validity of the superposition approximation also depends on χ . The value of the reduced potential for any system depends upon the temperature, and as far as the equations of the theory are concerned (neglecting now a physical interpretation) any actual temperature change can, according to (4.8), be compensated by a suitable hypothetical readjustment of the actual particle interaction potential. If the temperature of the real physical system is T_R , then the corresponding reduced potential is $\chi_R = \psi/kT_R$. Any variation of temperature or interparticle force potential from the values found in the actual system can be described by introducing a coupling parameter γ such that the reduced potential for the modified system, χ , is written $\chi = \gamma\chi_R$. γ is a continuous function in the range zero to unity so that the range $0 \leq \gamma \leq 1$ corresponds to the range $0 \leq \chi \leq \chi_R$: for the temperature there is also the associated range $T_R \leq T \leq \infty$.

When $\gamma = 0$ the particles all move independently with no mutual interaction; when $\gamma = 1$ the coupling is complete as in the actual system. The variable coupling applies equally to all particles simultaneously and in this respect differs from the earlier work of Kirkwood and Boggs (1942) who allowed the coupling between only one selected particle and the remainder to be varied. Any variation of the coupling between the particles will cause changes in the various distribution functions which can be calculated from the equations of § 4, such as (4.3) using (4.5), by inserting $\chi = \gamma\chi_R$ and then differentiating with respect to γ . Alternatively the equivalence $[T(\partial/\partial T) \sim -\gamma(\partial/\partial\gamma)]$ can be invoked in order that the effect of the variation in coupling can be inferred directly from (4.12). Using either of these methods the value of the h th order distribution for the coupling parameter γ , written $n^{(h)}(\gamma)$, is related to that at $(\gamma + \Delta\gamma)$, written $n^{(h)}(\gamma + \Delta\gamma)$, according to

$$n^{(h)}(\gamma + \Delta\gamma) - n^{(h)}(\gamma) = \Delta\gamma \frac{\partial n^{(h)}(\gamma)}{\partial \gamma} + O(\Delta\gamma)^2 \quad \dots \quad (7.1)$$

provided $\Delta\gamma$ is sufficiently small†. The special cases $h = 2$ and $h = 3$ are of especial importance in the theory of liquids, and for these cases we have

$$\begin{aligned} - \frac{\partial n^{(2)}(\mathbf{r}_1, \mathbf{r}_2; \gamma)}{\partial \gamma} &= n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) [\chi_R(\mathbf{r}_1, \mathbf{r}_2) + \mathcal{A}_R] + n \int \left(\sum_{i=1}^2 \chi_R(\mathbf{r}_1, \mathbf{r}_3) \right) \\ &\quad \times n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) d\mathbf{r}_3 + n^2 \iint \chi_R(\mathbf{r}_3, \mathbf{r}_4) n^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) \\ &\quad \times d\mathbf{r}_3 d\mathbf{r}_4 \equiv L_2[n^{(2)}, n^{(3)}, n^{(4)}; \gamma] \quad \dots \quad (7.2 a) \end{aligned}$$

† "Variation of interparticle coupling can be contemplated only for a physically realistic potential function which does not have singularities, e.g. at the origin."

$$\begin{aligned}
\text{and} \quad -\frac{\partial n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3; \gamma)}{\partial \gamma} &= n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \left[\left(\sum_{i=1}^3 \sum_{j>i}^3 \chi_R(\mathbf{r}_i, \mathbf{r}_j) \right) + \mathcal{A}_R \right] \\
&\quad + n \int \left(\sum_{i=1}^3 \chi_R(\mathbf{r}_i, \mathbf{r}_4) \right) n^{(4)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) d\mathbf{r}_4 \\
&\quad + n^2 \iint \chi_R(\mathbf{r}_4, \mathbf{r}_5) n^{(5)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4, \mathbf{r}_5) d\mathbf{r}_4 d\mathbf{r}_5 \\
&\equiv L_3[n^{(3)}, n^{(4)}, n^{(5)}; \gamma]. \quad \dots \quad (7.2b)
\end{aligned}$$

In these equations \mathcal{A}_R is obtained from (4.13) by replacing χ with χ_R . The right-hand side in each case, which respectively defines the two functions L_2 and L_3 , is to be evaluated for the value γ of the coupling parameter. By treating an extended increment of γ , $d\gamma$ say, as the sum of elementary increments $\Delta\gamma$ the formulae (7.1) and (7.2) have more general application. The temptation to insert the three formulae (5.1), (5.2) and (5.3) directly into the expressions (7.2) will for the present be resisted.

7.2. Inappreciable Coupling

In one limiting case the formulae of § 4 can be directly evaluated to yield the distribution functions as function of the interparticle pair forces; this is the case of very small interparticle coupling (γ small, virtually zero). If χ appearing in (4.5) is sufficiently small then the integrations in (4.3) can be conducted in practice because cross correlations (square and higher powers together with cross products of the potentials) are negligibly small. For if $X \gg X^2$ the exponential term in (4.5) need be expanded only as far as the first term and the integrations associated with (4.3) evaluated directly to yield the distribution functions. Under these circumstances the pair and triplet distributions are given respectively by the expressions:

$$\begin{aligned}
(1+B)n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= 1 - \chi(\mathbf{r}_1, \mathbf{r}_2) - n \int \left(\sum_{i=1}^2 \chi(\mathbf{r}_i, \mathbf{r}_3) \right) d\mathbf{r}_3 - n^2 \\
&\quad \times \iint \chi(\mathbf{r}_3, \mathbf{r}_4) d\mathbf{r}_3 d\mathbf{r}_4, \quad \dots \quad (7.3a)
\end{aligned}$$

$$\begin{aligned}
(1+B)n^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= 1 - \sum_{i=1}^3 \sum_{j>i}^3 \chi(\mathbf{r}_i, \mathbf{r}_j) - n \int \left(\sum_{i=1}^3 \chi(\mathbf{r}_i, \mathbf{r}_4) \right) d\mathbf{r}_4 - \frac{n^2}{2} \\
&\quad \times \iint \chi(\mathbf{r}_4, \mathbf{r}_5) d\mathbf{r}_4 d\mathbf{r}_5 \quad \dots \quad (7.3b)
\end{aligned}$$

where

$$B = -\frac{n^2}{2} \iint \chi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad \dots \quad (7.3c)$$

The remaining lower order distributions can also be found but will not be written down here. A suitably critical test of the validity of these expressions is provided by invoking (4.4) with \hbar set equal to 2.

These expressions will be valid for all γ less than some special value γ_1 , say: thus the formulae (7.1) and (7.2) can be applied starting from values of $n^{(2)}$ and $n^{(3)}$ calculated for some γ in the range $0 \leq \gamma \leq \gamma_1$.

7.3. Use of the Parameter

It should be remembered here that our present concern is the accurate calculation of the pair distribution for a liquid, and the superposition approximation must be introduced as harmlessly as possible. This must dictate the way in which the eqns. (7.1), (7.2 *a*), and (7.2 *b*) are used. There are several possibilities, distinguished in application by the complexity of associated numerical evaluation and in results by the degree of influence of the superposition approximation; we consider these various theoretical possibilities now. It is convenient to order the discussion by using a scheme which successively frees the lower order distributions from the approximation.

7.3.1. Exact triplet

The expression (5.1) is not now to be invoked, although (5.2) and (5.3) are. The distributions $n^{(2)}$, $n^{(3)}$, $n^{(4)}$, and $n^{(5)}$ can be assumed known in the region of inappreciable coupling (i.e. for all $\gamma < \gamma_1$) and the equations of the theory used to determine $n^{(2)}$ for the limiting and physically important case of $\gamma = 1$.

It is known from the numerical work of Kirkwood *et al.* (1952) that the insertion of (5.1) into (6.1), arranged to apply to central forces, and with $\gamma = 1$, leads to significant data for liquid argon. Agreement with experiment must surely increase if the triplet distribution is freed from the superposition approximation even though the higher order functions are not. By starting the procedure at the point $\gamma = \gamma_1$, all the distribution functions can be assumed to be known analytically at this point. By using (7.2 *b*) the triplet distribution can be calculated for the coupling parameter $(\gamma_1 + \Delta\gamma)$, written $n^{(3)}(\gamma_1 + \Delta\gamma)$. Inserting this value on the right hand of eqn. (6.1), and writing for the reduced potential the quantity $(\gamma_1 + \Delta\gamma)\chi_R$ throughout, there results a linear inhomogeneous equation whose solution is $n^{(2)}(\gamma_1 + \Delta\gamma)$, and which reduces to a scalar equation in the special case of spherical particles. The boundary condition (4.14 *a*) is also to be invoked. The functions $n^{(4)}$ and $n^{(5)}$ applying at $(\gamma_1 + \Delta\gamma)\chi_R$ can be obtained from the calculated pair and triplet functions using (5.2) and (5.3). All is then known for the procedure to be applied to the next interval $\Delta\gamma$. If the subscript zero is applied to a distribution to denote the use of the superposition approximation, the procedure outlined above can be expressed mathematically in the following way. It is assumed that the functions $n^{(2)}(\gamma)$ and $n^{(3)}(\gamma)$ are known, where γ lies in the range $\gamma_1 \leq \gamma \leq 1$. Then $n^{(3)}(\gamma + \Delta\gamma)$ follows from (7.1) and (7.2 *b*):

$$n^{(3)}(\gamma + \Delta\gamma) = n^{(3)}(\gamma) + \Delta\gamma L_3[n^{(3)}(\gamma), n_0^{(4)}, n_0^{(5)}; \gamma] + 0(\Delta\gamma)^2. \quad (7.4)$$

The pair distribution $n^{(2)}(\gamma + \Delta\gamma)$ is then derived from (6.1) which can be written in the obvious shorthand form:

$$\mathcal{L}^{(1)}[n^{(2)}(\gamma + \Delta\gamma); (\gamma + \Delta\gamma)\chi_R] = \mathcal{C}_1[\mathbf{r}_1, \mathbf{r}_2; n^{(3)}(\gamma + \Delta\gamma), (\gamma + \Delta\gamma)\chi_R]. \quad (7.5)$$

In (7.5) the left-hand side is an operator notation standing in place of the left-hand side of (6.1), while the right-hand side is a function of the relative configuration of the particle pair and stands in place of the right-hand side of (6.1). The boundary condition $n^{(2)}(r_{12}) \rightarrow 0$ as $r_{12} \rightarrow 0$ is to be applied at each stage of the process which is repeated using suitable intervals until the case $\gamma = 1$ is solved. Using this method data for the pair distribution is determined without the need to invoke the superposition approximation directly to the triplet distribution in the form (5.1). The great drawback of any application of this procedure, even to simple liquids for which (4.9) is valid, is the large amount of numerical work that would be involved, even though each operation involves only elementary mathematics. An attractive merit of the method is that the superposition approximation is not explicitly used in the equation from which $n^{(2)}$ itself is calculated.

An obvious modification of this procedure is the substitution of (7.2a) in place of (7.5) for the actual determination of $n^{(2)}$. Although it is not now necessary to solve a first-order equation it is necessary to invoke the superposition approximation explicitly (for the quadruplet function) in the equation determining the pair distribution. Thus the approximation is now invoked one time more than in the procedure using (7.3) and (7.4).

7.3.2. *Extension to higher order functions*

In principle, and in practice also for sufficiently powerful supporting numerical computational aids, the arguments of the last paragraph can be extended to free the remaining lower order distributions from the superposition approximation. The eqn. (7.1) is applied to the quadruplet distribution by writing $h = 4$. The equation to supplement (7.2a) and (7.2b), relating $\partial n^{(4)}/\partial \gamma$ to the functions $n^{(4)}$, $n^{(5)}$ and $n^{(6)}$, can be obtained directly from (4.3) and (4.5) by differentiation with respect to γ , or alternatively from (4.12) using the previously noted correspondence between T and γ . The superposition approximation is now to be applied to $n^{(5)}$ and $n^{(6)}$, but not to either $n^{(3)}$ or $n^{(4)}$. With $n^{(3)}$ and $n^{(4)}$ known at each value of γ there are three possibilities for the calculation of $n^{(2)}$.

One is the insertion of $n^{(3)}$ into the procedure involving (7.4) and (7.5): the triplet distribution now is more accurate since it does not involve the use of the superposition approximation even in the form (5.2). Alternatively the method can proceed with the second-order equation (6.3) replacing (6.1), the right-hand side of the equation not involving the superposition approximation explicitly. There is the remaining alternative of calculating $n^{(2)}$ directly from (7.2a): here the superposition approximation does not explicitly appear in the expression. Although it can be expected that these methods will in application lead to improved accuracy in data for the pair distribution, the extreme complexity of any calculations associated with their use makes them of interest at the present time largely for completeness in the theory.

Further extension of the arguments can be contemplated which successively free the lower order distribution functions from the superposition approximation. In principle the effect of the approximation can be continuously decreased by this procedure which is broadly related to the problem of evaluating the partition function by using controlled approximations. In practice, at the present time, the numerical complications are likely to preclude distribution functions other than the triplet from being specified without explicitly invoking the superposition approximation. Nevertheless even this step can be expected to yield important improvements in the accuracy of the calculated pair distribution.

7.3.3. *Physical value*

It remains to assess the physical validity of the mathematical method of the variable coupling considered in the present section. Any artificial and hypothetical tempering with the actual reduced potential function applying to the real system of interest must be carefully considered when any calculated data are compared with those obtained experimentally. Objections can be raised to essentially all theories of gross matter based on a particle-in-a-box model, and can be assessed finally only by a careful study of the calculated data: the variable coupling method is no easier to assess. Because the arguments of the present section have not been used in any numerical calculations, and analytic discussion is not possible in other than very broad terms, any such discussion can be pursued at present in cursory fashion only.

Two considerations are perhaps pertinent here. First, the method is mathematical and involves the gradual introduction of the reduced potential. It is not unreasonable to expect that the method will converge to yield the same data as that given by the theory in a form which accounts for the full effect of the potential from the outset.

Second, the calculations move over the full fluid range starting with conditions appropriate to the dilute gas (negligible coupling) passing through all stages to those of a condensed system of particles (full coupling) which is to be identified with the liquid. But this full range is made at constant number density, and on physical grounds the process is unusual. Nevertheless it was realized in §7.1 that any variation of the reduced potential can be regarded alternatively as a hypothetical change of the actual potential of interaction or as a real change of temperature. The calculations using variable coupling, can, therefore, be treated as providing information of the dependence of the uniform pair distribution on temperatures at constant volume, and particle number. Because the arguments and equations of §4 apply to all equilibria, and in particular to the liquid-vapour region, it might be expected that the equations themselves will correct at least crudely for any non-liquid features which might tend to appear before the coupling becomes strong. The situation is helped by the fact that the liquid and vapour regions have no sharp separation such as is found between the solid and liquid regions of a simple substance.

In summary it can be said that the arguments of the present section would seem to provide a method of reducing the effect of the superposition approximation upon the calculations of the structure of a liquid. Any more definite critique of the method would seem of necessity to involve actual calculations based upon data appropriate to an actual simple liquid whose properties are well known experimentally, such as liquid argon.

§ 8. THE PAIR DISTRIBUTION AND THERMODYNAMICS

Up to this point the discussion has centred around the determination of the structure of a uniform liquid whose volume is sufficiently great to allow any effects of the boundaries to be neglected. It is not proposed to enter here into any discussion of the boundary region, where conditions are complex and far from clear, since it is found in practice that laboratory liquid specimens that are not too small behave as if they were microscopically indefinitely large.

According to the elementary notions collected in § 2 and the results quoted in § 3, the liquid structure can be adequately described theoretically by the pair distribution which may be calculated using the arguments of the preceding sections. It remains now only to relate this theoretical knowledge of liquid structure to the macroscopic liquid properties familiar in gross matter. In direct terms this means relating the thermodynamic functions to the pair distribution. Although the details of this relation are well known it is convenient, (see e.g., de Boer 1948) for reasons for completeness, briefly to collect them together again here. These formulae are of crucial importance to the theory just set down, since any final conclusion as to the adequacy of the pair distribution for the description of the liquid state must centre on a comparison between the calculations based on these formulae and the corresponding experimental data.

According to the well-established principles of classical statistical mechanics (Tolman 1938, Eisenschitz 1950) the free energy F of any equilibrium system is related to the partition function Z of the representative particle model, and defined by eqn. (4.6), according to

$$F = -kT \log [(2\pi M kT)^{3N/2} Z] \quad . \quad . \quad . \quad . \quad (8.1)$$

where M is the particle mass. Macroscopic thermodynamics (Fermi 1956), again applying to any equilibrium system, can be fully summarized by a single relation between the internal energy, U , the entropy, S , and the temperature, viz.:

$$F = U - TS. \quad . \quad . \quad . \quad . \quad . \quad (8.2)$$

The free energy is a function of the volume, temperature, and pressure, p , so that the thermodynamic variables U , S and p can be expressed in terms of Z using (8.1) and (8.2).

For the internal energy and pressure it is found that (Tolman 1938):

$$\left. \begin{aligned} (a) \quad U &= kT^2 (\partial/\partial T) \{ \log [(2\pi M kT)^{3N/2} Z] \}, \\ (b) \quad p &= kT (\partial/\partial V) \{ \log [(2\pi M kT)^{3N/2} Z] \}. \end{aligned} \right\} \quad (8.3)$$

Unfortunately these formulae are not of direct value for liquids because, as was seen earlier, the partition function in configuration space cannot be evaluated in this case. Instead it is necessary to rearrange these formulae into a form which depends explicitly on the pair distribution†.

Consider first the internal energy which can be expanded to the form :

$$U = kT^2 \frac{\partial}{\partial T} \left[\log (2\pi Mk)^{3N/2} + \frac{3N}{2} \log T \right] + kT^2 \frac{\partial}{\partial T} (\log Z). \quad (8.4)$$

The first term on the right-hand side is simply $(\frac{3}{2})NkT$ while the second term is $kT^2 Z^{-1} (\partial Z / \partial T)$. Because the total potential Ψ is temperature independent, it is found that this expression, written in terms of the pair distribution, is :

$$(kT/2) \int \int n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \chi(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2.$$

For the case of spherical particle symmetry, then, the internal energy is given by the expression :

$$U = \frac{3NkT}{2} + \frac{kT}{2} \int_0^\infty n^{(2)}(r) \chi(r) 4\pi r^2 dr \quad . \quad . \quad (8.5)$$

where r is the pair separation distance. This relation is exact, within the limits of validity of (4.9), no terms having been neglected.

The rearrangement of the expression for the pressure, (8.3*b*), is not so straightforward since a volume differentiation is involved which affects the limits of integration of the partition function. Green (1947) showed how this difficulty can be overcome by the introduction of a characteristic length : alternatively de Boer (1948) avoided the direct use of (8.3*b*) by invoking the virial theorem. Applying this theorem to a closed volume V it follows that the product of volume and pressure is given by :

$$pV = NkT - \frac{kT}{N!Z} \int \dots \int \left\{ \frac{1}{6} \sum_{i=1}^N \sum_{j>i}^N \mathbf{r}_{ij} \frac{\partial \chi(\mathbf{r}_i, \mathbf{r}_j)}{\partial \mathbf{r}_{ij}} \right\} \exp \{-X\} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N.$$

The integral can be rearranged to include the pair distribution by using the equations of § 4 : for spherically central forces we obtain finally :

$$pV = NkT - \frac{kT}{6} \int_0^\infty n^{(2)}(r) \frac{\partial \chi(r)}{\partial r} 4\pi r^3 dr. \quad . \quad . \quad (8.6)$$

Again this expression is exact, no terms having been neglected.

† In contrast to this kinetic theory approach the cell model attempts to use the formulae (8.3) directly by avoiding the problem of the exact evaluation of the partition function. Instead, the value of Z is estimated using a suitable lattice-type model where the particle motion is restricted to a cell whose extent is dictated by the close distribution of neighbouring particles. Kirkwood (1950), and later Green (1956), have investigated the relation between the cell model and the correct kinetic theory.

In both expressions (8.5) and (8.6) the first term is well known in the theory of the dilute gas; the second term in each case involves the interaction between particle pairs and so is predominant in the liquid region. The expressions, therefore, can be expected to cover fully the range between the indefinitely dilute gas and the real liquid. A comparison between the numerical values of these expressions and experimental data allows the assertion to be tested that a knowledge of the pair distribution alone is sufficient for describing simple liquid structure.

Kirkwood *et al.* (1952) have applied these expressions to the case of liquid argon; in addition these authors also calculated other data such as the entropy excess of gas over liquid which will not be considered here. The agreement with experiment is not perfect, but is possibly as satisfactory as can be expected with the data calculated from (8.2) using the modified hard core model.

A numerical investigation of the eqns. (8.5) and (8.6) shows clearly a critical dependence on the fine details of the pair distribution, and it is in consequence essential to calculate this distribution on the basis of the correct pair interaction force. In particular the repulsive region of this force must be specified carefully. A real need exists at the present time for making precise calculations of the pair distribution on this understanding and so fully testing the theory against thermodynamic data derived from experiment.

§ 9. CONCLUSIONS

The present discussion of the theory of a simple liquid in equilibrium has been based on the now well accepted assertion that the liquid structure is adequately represented by the pair distribution. The plausibility and utility of this assertion were first explained and some of the methods which seem capable of providing this information theoretically by one consistent argument have been explored. In the last section the relation between the pair distribution and the thermodynamic functions was indicated, and data for liquid argon calculated by Kirkwood and his school were very briefly quoted. Although very much more numerical work still remains to be done the conclusion would seem to emerge that the theory has already provided interesting results, and is capable of providing an understanding of simple liquids at least.

It will be realized that much detailed theoretical work still remains to be done before this classical problem can be finally solved. In this connection electronic computers, used to conduct mathematical experiments in addition to simply solving equations, can be expected to play an important rôle in the future. At present the solutions of the equations of the theory are severely controlled by the superposition approximation: it can be hoped that the arguments of § 7 will ultimately alleviate this inadequate position for liquids. The calculations, even for simple liquids, can be expected to be severe even if only the triplet distribution is freed from the approximation, but the increased accuracy may well be significant. The thermodynamic data calculated from the standard formulae of § 8 are found in practice to be

very sensitive to the exact details of the pair distribution. While this provides a critical test of the theory of liquid structure the need to rearrange the thermodynamic data to reduce this sensitivity cannot be overlooked in ultimate practical applications of the theory.

The formulae of the theory apply generally to any molecular shape but the mathematical complexity is such that only spherically symmetric particles can be reasonably treated at the present time. There is a need for allowing details of assymetry to be accounted for in a quantitative way, although the arguments for spherical particles do give at least qualitative information for these more complex liquids.

It can, however, be said that the present application of statistical mechanics to equilibrium liquids, in which the short-ranged spatial order is described by the pair distribution, appears capable of leading to a fully adequate understanding of the structure of a uniform liquid.

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The Saturation Magnetostriction of Ferromagnetics

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§ 1. INTRODUCTION

1.1. *Magneto-elastic Effects*

THE elastic properties of a solid body may, in general, be characterized by a unique expression connecting the components of stress and strain at any point in the body. For many materials, however, notably the ferromagnetic metals and their alloys, the strain is also a function of the external magnetic field in which the body is placed. Conversely, the state of magnetization of such a body depends not only on the magnetic field but also on the stress components. The elastic and magnetic states of the body are thus interdependent and each is a function both of the field and of the stress. The subject of magnetostriction is concerned with the special case in which one of these external influences—the stress—is absent. In this case the

state of magnetization and the state of strain of the body are both dependent only on the external magnetic field and the former and latter quantities vary with field in a manner which defines respectively the magnetization and the magnetostriction.

In practice the state of magnetization is also influenced by the size and shape of the body, so that it is convenient to interpret magnetostrictive strains in terms of the magnetic state rather than the applied field. From the point of view of atomic interactions this is a more fundamental approach and, since the variation of the state of magnetization with applied field is well understood, no loss of generality results from this change. The basic problem is therefore to relate the observed magnetostrictive deformation which accompanies changes in the magnetic state of the body to the associated average intensity of magnetization, I . However, at every stage of the magnetization process, the body is subdivided into a number of domains each magnetized to the same saturation value, I_s , so that if the local magnetostriction were to depend only on the magnitude of the local magnetization no deformation would accompany a rearrangement of these domains. It is therefore necessary to assume that the magnetostrictive strain which accompanies the magnetization to saturation of an elementary region of the body is anisotropic and depends on the orientation of the magnetization vector with respect to the crystallographic axes associated with this region. The magnetostrictive deformation of the body as a whole, i.e. the bulk magnetostriction, is thus explained by postulating that in each domain the establishment of the spontaneous magnetization is accompanied by the appearance of an anisotropic deformation of the domain and this deformation is referred to as the spontaneous magnetostriction.

The dependence of the spontaneous magnetostriction on the direction of magnetization within a domain may be directly correlated with the bulk magnetostriction and magnetization of the body provided that the crystallographic axes retain the same directions for every domain. A single crystal specimen must therefore be employed and it is with such specimens that the present account is primarily concerned. Whatever the state of magnetization of the crystal, the observed bulk magnetostriction may be interpreted in terms of the spontaneous magnetostriction of each domain, but this interpretation is both simple and unambiguous only when the crystal is magnetized as a single domain. This situation may be produced without the use of very intense applied fields provided that the magnetic field acting within the body is uniform throughout the volume of the crystal. Thus, if the specimen is situated in a uniform external magnetic field, the demagnetizing field must also be uniform and for this condition to be satisfied the crystal boundary must be a complete surface of the second degree. The only case in which such a body is of finite dimensions is when it is ellipsoidal in shape. The use of such a specimen ensures that the strain components are the same at every point in the body and this limitation greatly simplifies the determination of the form of the spontaneous magnetostriction. A further simplification is afforded by the fact

that the purely anisotropic part of the spontaneous magnetostriction is small, the associated lattice strain usually being considerably less than one part per thousand.

In § 1.2 an expression is derived for the spontaneous magnetostrictive strain in a cubic crystal, referred to an undeformed crystal lattice in which the magnetic interactions have been annihilated. This state, in which there are no magnetic interactions to deform the crystal, is not, of course, realizable experimentally but it is shown in § 1.3 that there are in fact several ways of estimating the lattice deformation associated with the destruction of the spontaneous magnetization. In practice, however, it is not necessary to define this hypothetical initial state more exactly since, due to the presence of the spontaneous magnetostriction, experimental measurements of strain always refer to two or more *deformed* states of the crystal and interest is centred mainly in the lattice strain which accompanies a variation in the direction in which the crystal is magnetized to saturation.

Although the observed saturation magnetostriction of single crystals conforms closely to the expression for the spontaneous magnetostriction mentioned above, there is often a small difference between these quantities which indicates that the deformation of the crystal does not arise wholly as a direct result of the occurrence of the spontaneous magnetization. The explanation of this effect is to be found in the interaction of the demagnetizing field with the spontaneous magnetization. Since the demagnetizing energy depends upon the shape of the specimen, it may be decreased by a deformation of the body. It is thus to be expected that the strain dependence of the demagnetizing energy will give rise to an additional lattice strain and this phenomenon is known as the form effect. The contribution of the form effect to the magnetostriction is usually small but for accurate work it should not be ignored. The form effect is considered in detail in § 2.4.

1.2. *The Spontaneous Magnetostriction of Cubic Crystals*

The method adopted to obtain a formal expression for the spontaneous magnetostriction is to represent the associated lattice strain in terms of successively increasing powers of $\alpha_1, \alpha_2, \alpha_3$, the direction cosines of the spontaneous magnetization referred to coordinate axes coinciding with the crystallographic axes of the undeformed cubic crystal. Since the lattice strain is small and homogeneous the form of the resulting expression is dictated entirely by the requirements of crystal symmetry.

In order to describe the deformation of the crystal, an arbitrary point, P , defined in the undeformed lattice by the coordinates x_1, x_2, x_3 , may be assumed to undergo a displacement u_1, u_2, u_3 . The point x_i thus moves to $x_i + u_i$ whilst the displacement of a neighbouring point $x_i + \Delta x_i$ is $u_i + \Delta u_i$. Since these displacements are small, the Δu_i may be written in the form

$$\Delta u_i = \frac{\partial u_i}{\partial x_j} \Delta x_j, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which the occurrence of a repeated suffix indicates summation in the conventional manner. The strain tensor $e_{ij} = \partial u_i / \partial x_j$ may be separated into its symmetrical and antisymmetrical parts, the latter representing a rotation of the crystal as a whole without any deformation of the lattice. The former is the symmetrical strain tensor $E_{ij} = \frac{1}{2}(e_{ij} + e_{ji})$ which characterizes a pure deformation and represents the distortion of the crystal in the neighbourhood of the point P . Since the strain is homogeneous the components E_{ij} are constants of the crystal which do not depend upon position so that the lattice strain in the direction of the element Δx_i , as measured by any of the more usual mechanical methods, may be written

$$\lambda = \Delta u_i \Delta x_i / \Delta x_j \Delta x_j. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Introducing the direction cosines of the measuring direction, $\beta_i = \Delta x_i / \sqrt{(\Delta x_j \Delta x_j)}$, the strain in the direction β , associated with magnetization in the direction α , becomes

$$\lambda = e_{ij} \beta_i \beta_j = E_{ij} \beta_i \beta_j, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where the E_{ij} are functions only of the α_i . If the lattice strain is investigated by means of a strain gauge cemented to the crystal then the gauge accommodates itself to the true deformation of the lattice. Thus the relative orientation of the measuring direction and the crystal lattice is preserved and the corresponding quantity which is measured is $\lambda = \sqrt{(\Delta u_i \Delta u_i / \Delta x_j \Delta x_j)}$ which differs from $E_{ij} \beta_i \beta_j$ only by negligible terms involving products of the E_{ij} .

The dependence of the E_{ij} upon the direction α may now be introduced by expressing λ as a power series in the α_i with terms of the form $f(\alpha_1, \alpha_2, \alpha_3) \beta_i \beta_j$. However, the requirements of cubic symmetry ensure that each term must be even in the α 's and β 's separately, unaltered by the interchange of any pair of suffixes in the α 's and β 's simultaneously and unaltered by the simultaneous change of sign of any pair $\alpha_i \beta_i$. Thus there are, for example, only six possible terms of the second order in the α 's, namely $\alpha_1^2 \beta_1^2$, $\alpha_2^2 \beta_2^2$, $\alpha_3^2 \beta_3^2$, $\alpha_1 \alpha_2 \beta_1 \beta_2$, $\alpha_2 \alpha_3 \beta_2 \beta_3$ and $\alpha_3 \alpha_1 \beta_3 \beta_1$. From symmetry considerations they may be grouped together into two terms, $S(\alpha_1^2 \beta_1^2)$ and $S(\alpha_1 \alpha_2 \beta_1 \beta_2)$, with different coefficients, where here as throughout, the operator $S()$ denotes the sum of the three quantities obtained by a cyclic permutation of suffixes on the expression within the brackets.

The linear dependence of λ on the two quantities $S(\alpha_1^2 \beta_1^2)$ and $S(\alpha_1 \alpha_2 \beta_1 \beta_2)$ was first proposed by Akulov (1928, 1930) and the analysis was later extended by Gans and von Harlem (1933) to include terms of fourth order in the α 's. More recently Vautier (1954) has deduced the form which the expression for λ assumes when all the possible terms of less than eighth order in the α 's are included. When a superfluous term in $S(\alpha_1^6)$ is omitted, this expression may be written in the form

$$\begin{aligned} \lambda = & A_0 + A_1 S(\alpha_1^2 \beta_1^2) + A_2 S(\alpha_1 \alpha_2 \beta_1 \beta_2) + A_3 S(\alpha_1^2 \alpha_2^2) \\ & + A_4 S(\alpha_1^4 \beta_1^2) + A_5 S(\alpha_1 \alpha_2 \alpha_3^2 \beta_1 \beta_2) + A_6 S(\alpha_1^6 \beta_1^2) \\ & + A_7 S(\alpha_1^3 \alpha_2^3 \beta_1 \beta_2) + A_8 S(\alpha_1 \alpha_2 \alpha_3^4 \beta_1 \beta_2) + A_9 \alpha_1^2 \alpha_2^2 \alpha_3^2. \quad . \quad . \quad (4) \end{aligned}$$

It is possible, in principle, to expand λ even further in ascending powers of the α 's but higher order terms tend to make λ oscillate rapidly with the angular orientation of the direction of magnetization. Since this is contrary to experiment, it is reasonable to expect the coefficients of such terms to be small. Although the recent work of Baltzer (1957) has emphasized that it is sometimes necessary to employ eqn. (4) rather than an equation of lower order, it may be seen that the inclusion of so many independent constants must necessarily limit its usefulness. The justification for terminating the series at any stage of the expansion must always rely upon a comparison with the experimental data since the coefficients occurring in (4) are purely formal and subject only to the limitations of symmetry. This difficulty is considered in more detail in § 1.3 where the origin of the spontaneous magnetostriction is discussed. A comparison with the experimental data is attempted in § 2.5 and § 2.6. Finally, it may be mentioned that the arguments adduced above invoking considerations of symmetry to simplify the expression for λ neglect the fact that the symmetry of the lattice is actually lower than cubic as a result of the deformation of the crystal. This objection is dealt with in § 2.2 where a more rigorous derivation of eqn. (4) is advanced. This derivation is extended to hexagonal crystal lattices in § 2.3.

1.3. *The Origin of the Spontaneous Magnetostriction*

However accurately the spontaneous magnetostriction of actual materials may be represented by an equation of the form $\lambda = P_i S_i$, e.g. by eqn. (4), the coefficients P_i are as yet entirely empirical and they have not been related to the fundamental interatomic forces which result in the appearance of the spontaneous magnetization. If the origin of the spontaneous magnetostriction is investigated in more detail, it is found that the P_i depend upon the elastic constants of the material and also upon the coefficients of a power series in the α_i which represents the rate of change of anisotropy energy with strain. These latter coefficients may be referred to as the magneto-elastic coupling constants and it is shown in § 2 that the P_i may, in general, be expressed as the sum of a number of terms each of which is a numerical factor times the product of an elastic coefficient and a magneto-elastic coupling constant. It therefore follows that if the anisotropy energy does not depend upon the deformation of the crystal, there will be no spontaneous magnetostriction. If, however, the strain dependence of the anisotropy energy is non-zero then, when the crystal is magnetized, the lattice will deform spontaneously so as to lower the anisotropy energy. This deformation is, of course, opposed by elastic forces so that the equilibrium lattice strain occurs when there is an exact balance between the elastic and magnetic forces, corresponding to a minimum in the sum of the elastic and anisotropy energies. It may thus be seen that any physical theory of anisotropy in terms of interatomic interactions automatically permits the constants P_i to be evaluated. Unfortunately, however, there is at present no adequate physical theory of anisotropy in existence. Nevertheless, a

certain simplification may be effected if the P_i are expressed formally in terms of the empirical magneto-elastic coupling constants. These expressions are derived in § 2.2 and § 2.3 for cubic and hexagonal crystals respectively.

The spontaneous magnetostriction constants may be considered to fall into four distinct classes depending upon the forms of the associated angular functions S_i . For example, in eqn. (4) all the constants except A_0 , A_3 and A_6 are coefficients of terms which are anisotropic with respect to both the directions α and β . These constants may therefore be conveniently designated anisotropic-anisotropic constants and their existence gives rise to the spontaneous magnetostriction as usually observed. The constants A_3 and A_6 , being independent of the β_i , are anisotropic-isotropic and they are thus associated with an isotropic deformation of the crystal, i.e. a change in volume. Since both sets of constants are coefficients of terms which depend upon the α_i , these A_i may be evaluated experimentally by measuring the variation of λ with the α_i for fixed values of the β_i . The A_i may then be determined by a method which is considered in detail in § 2.6. The remaining spontaneous magnetostriction constant, A_0 , is isotropic-isotropic. For cubic crystals it has been stated (Fowler 1936) that A_0 may be a function of the β_i . However, λ is quadratic in the β_i so that the only permissible function of the β_i consistent with the cubic symmetry of the crystal is $S(\beta_1^2)$ which is identically equal to unity. It may therefore be seen that the constant A_0 is isotropic-isotropic for a cubic crystal although for crystals of lower symmetry isotropic-anisotropic terms may occur. The most obvious method of evaluating the constant A_0 is to measure the thermal expansion of the crystal over a temperature range which includes the Curie point. The deformation of the crystal associated with the appearance of the spontaneous magnetization may then be seen superimposed on the normal thermal expansion. There are at least two indirect methods of estimating A_0 . One which involves measuring the rate of change with magnetic field of the saturation magnetization and of the fractional change in volume of a polycrystal (Lee 1955 a) gives values of A_0 which are in general agreement with those obtained from thermal expansion measurements. A second method in which the lattice constant of a binary alloy, one component of which is the ferromagnetic metal under consideration, is measured over a range of composition which includes that of an alloy with the Curie point at room temperature (Köster and Schmidt 1934) gives values of A_0 which are not usually in agreement with the preceding two methods. The reason for this discrepancy is unknown. A more detailed consideration of the isotropic-isotropic part of the spontaneous magnetostriction is presented in § 4.3 and it is only necessary, at this point, to note that experiments on cubic materials show the spontaneous magnetostriction to be chiefly an isotropic change in volume associated with the term A_0 , this coefficient being much larger than the other spontaneous magnetostriction constants. However, owing to the presence of the spontaneous magnetization even in the demagnetized state, the contribution of A_0 to λ is not normally observed

and the spontaneous magnetostriction manifests itself as the much smaller anisotropic effect associated with the remaining A_i . One magneto-elastic coupling constant is also much larger than the others and the numerical values of these constants are evaluated for the common ferromagnetic metals in § 4.3.

1.4. Factors Affecting the Magnetostriction Constants

The derivation of an equation for the spontaneous magnetostriction, λ , advanced in § 1.2 entails the implicit assumption that the magnitude of the saturation magnetization vector is constant for a given material since λ is expressed in terms of the direction cosines α_i rather than the components $I_s\alpha_i$. In practice, however, above the point of technical saturation, both λ and I_s exhibit a weak dependence on the applied magnetic field, H : the dependence of λ on H is linear and is known as the forced magnetostriction. The spontaneous magnetostriction is a function of both the magnetization and the applied field and therefore the spontaneous magnetostriction coefficients P_i are also functions of both I_s and H . However, in high fields the magnetization and applied field are co-directional so that, since I_s is a unique function of H for a particular specimen, the spontaneous magnetostriction may be represented as a function of the applied field only. Since the forced magnetostriction as observed experimentally is a small and linear effect, usually of the order 10^{-10} oersted $^{-1}$, the spontaneous magnetostriction in high fields may be represented by the first two terms of a Taylor expansion in H of $P_i S_i$ about a constant value of field, H_c . Thus for applied fields greater than the value, H_s , needed to produce technical saturation

$$\lambda = P_i S_i = (P_i)_{H_c} S_i + P_i'(H - H_c) S_i, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the forced magnetostriction constants P_i' are the partial derivatives of the corresponding P_i with respect to H . Experimental measurements of the variation of strain with H in high fields yield apparent values of the coefficients occurring in eqn. (5) rather than true values since the contribution of the form effect must be added to λ to obtain the total deformation of the specimen. However, the observed values of the $(P_i)_{H_c}$ may be readily corrected for the contribution of the deformation due to the form effect which is considered in detail in § 2.4. Further, it is shown in § 4.1 that the apparent values, $(P_i')_a$, and the true values, P_i' , of the forced magnetostriction constants differ by quantities which may, in general, be neglected.

For any particular specimen the various values of $(P_i)_{H_c}$ corresponding to different values of H_c may be compared by determining the value appropriate to zero external field from an extrapolation of the linear portion of the P_i versus H curve to $H = 0$. When values of P_i are quoted without a reference value of H , it is usually assumed that they have been obtained in this manner. Although it appears to be a common practice, this method suffers from the disadvantage that data obtained with specimens of different shapes cannot be immediately compared because of the effect of the demagnetizing field. It would therefore appear that a more satisfactory

procedure would be to extrapolate the P_i versus H curves to the largest value of H at which the internal magnetic field, X , is zero. The values of P_i thus obtained should be the same for specimens of different shapes since they correspond to the 'true' value of the spontaneous magnetization (which may be obtained in a similar manner). In practice, both the demagnetizing field and the forced magnetostriction are often small compared with I_s and λ respectively. In such circumstances the distinction between the two extrapolated values of P_i loses much of its importance.

A more satisfactory formulation of eqn. (5) may be obtained by expanding $P_i S_i$ as the first two terms of a Taylor series in X , the internal field. For applied fields greater than H_s the spontaneous magnetostriction may thus be represented by

$$\lambda = (P_i)_{X_c} S_i + P_i'(X - X_c) S_i, \quad \dots \dots \dots (6)$$

where X_c is the value of the internal field when $H = H_c$. The advantage of this formulation over that of eqn. (5) is that the $(P_i)_{X_c}$ are now unique functions of X and are independent of the shape of the specimen. When $X_c = 0$ the coefficients $(P_i)_{X_c}$ may be identified with the values obtained, as mentioned above, by extrapolating the P_i versus H curves to the largest value of H at which the internal field is zero.

Another important way in which the values of the saturation magnetostriction constants may be varied is by the effect of a change in temperature. At present, a detailed theoretical prediction of the form of the variation of magnetostriction with temperature is impossible; nor is it possible to predict the temperature variation of either the elastic coefficients or the magneto-elastic coupling constants. In addition, none of the theoretical evaluations (Vonsovsky 1940, Katayama 1951, Fletcher 1955) of the saturation magnetostriction constants has proved conspicuously successful. A Taylor expansion of λ in terms of temperature, similar to eqn. (5), would be of little value since the magnetostriction is not, in general, a linear function of temperature. It would therefore appear that experimental work on this problem would be of considerable value, since the accumulation of sufficient data may suggest a more successful theoretical approach. It is also evident that such experimental work should ideally be coupled with the determination of the temperature variation of the elastic coefficients of the materials under investigation.

§ 2. THE MAGNETOSTRICTION OF SINGLE CRYSTALS

2.1. Introduction

When a ferromagnetic crystal is magnetized to saturation by a magnetic field of constant magnitude, the total lattice strain is the resultant of the spontaneous magnetostriction and the form effect, the deformation of the lattice being opposed in both cases by purely elastic forces only. The equilibrium deformation of the crystal may therefore be found by minimizing the sum of the magnetic and elastic energies with respect to the components of strain, E_{ij} . Since the spontaneous magnetostriction and the form effect are both small, they may be considered to be independent of each

other so that the equilibrium components of strain may each be expressed as the sum of two equilibrium components E_{ij}^v and E_{ij}^w associated respectively with these two effects. Thus the E_{ij}^v may be found by minimizing the sum of the elastic energy density, U , and the anisotropy (magneto-crystalline) energy density, V , whilst the E_{ij}^w correspond to a minimum value of $(U+W)$ where W is the demagnetizing energy density. The quantities U , V and W are all defined as energy densities referred to the volume of the original undeformed crystal. The E_{ij}^v and the E_{ij}^w are both functions of the temperature of the specimen and of the applied magnetic field. It is not customary, however, to refer measurements of the spontaneous magnetostriction to particular values of applied field. It is usually assumed that values appropriate to zero field have been obtained by linear extrapolation of the curves of forced magnetostriction versus field. The form effect is, in general, small compared with the spontaneous magnetostriction and its variation with field may be neglected as stated in § 1.4. To obtain expressions for the spontaneous magnetostriction and the form effect it is thus necessary to investigate the dependence of U , V and W upon the elastic and magnetic states of the crystal, i.e. upon the E_{ij} and the α_i .

According to the classical theory of elasticity (Love 1944) a linear relation exists between the components of stress and strain which may either be written in the form

$$T_{ij} = C_{ijkl} e_{kl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

or in the reciprocal form

$$e_{ij} = S_{ijkl} T_{kl}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$

where the C_{ijkl} are the elastic stiffness constants and the S_{ijkl} the elastic compliance moduli. As indicated in § 1.2, any homogeneous strain may be analysed into a pure strain and a rotation. The latter is ignored in formulating the stress-strain relationships. In addition it is assumed that the tractive forces acting on elements of area in the solid are so related that no torques tending to rotate the volume elements of the crystal are present. Provided that these assumptions are made, the generalized Hooke's law (7) is simplified by the relations $T_{ij} = T_{ji}$ and $e_{ij} = e_{ji} = E_{ij}$. Recent work by Laval (1951 a, b, 1954 a, b) has, however, cast doubt on the validity of these relations when either the static or the dynamic properties of crystals are under consideration. Le Corre (1953 a, b, c, 1954 a, b, 1955) has extended and developed Laval's approach and has given the complete schemes of the elastic coefficients for all the crystal classes. This work has been confirmed by Raman and Viswanathan (1955) and it now appears that cubic crystals such as iron and nickel are characterized by four independent elastic coefficients whilst eight coefficients are necessary to describe the elastic properties of hexagonal crystals such as cobalt and gadolinium. Although it has been suggested (Joel and Wooster 1958) that, in crystals subject to mechanical strains only, these numbers may be reduced to three and six respectively, it may nevertheless be concluded that the methods of the classical theory of elasticity are not applicable to the general case of

heterogeneous strain. Furthermore, since only infinitesimal strains are considered in the developments mentioned above, the modifications which must be made to the classical theory are of a different nature from those encountered when the deformation of the body is considered to be finite. If the classical approach is to be used to evaluate the spontaneous magnetostriction and the form effect then it is necessary to ensure that, in addition to the deformation being small, it is also the same at every point in the body, for it is only in this case that the relations $T_{ij} = T_{ji}$ and $e_{ij} = E_{ij}$ regain their validity. This homogeneity of strain may be achieved by employing ellipsoidal specimens as discussed in § 1.1. In addition, the elastic energy must also be referred to a state of homogeneous strain and in selecting experimentally determined values of the elastic coefficients preference should therefore be given to those determined by static methods. In recent work the emphasis has been on high-frequency methods of determining these coefficients but it should be remembered that in any dynamic experiment the strains are necessarily heterogeneous and the internal stress system may involve torques as well as tractive forces.

If $T_{ij} = T_{ji}$ and $e_{ij} = E_{ij}$, the stress and strain tensors both have only six independent components and a considerable simplification may be effected by replacing the full tensor notation with a new (matrix) notation using a single suffix running from one to six, according to the following scheme,

Old notation	E_{11}	E_{22}	E_{33}	E_{23}, E_{32}	E_{31}, E_{13}	E_{12}, E_{21}
New notation	E_1	E_2	E_3	$\frac{1}{2}E_4$	$\frac{1}{2}E_5$	$\frac{1}{2}E_6$

The factors of $\frac{1}{2}$ are necessary if the elastic energy is to be written in a compact form as the sum of similar terms, that is if full advantage is to be taken of the summation convention. It may be noted in passing that E_4, E_5, E_6 , as defined above, are equal to the 'engineering' shear strain components. In a similar way the stress components T_{ij} and the elastic stiffness constants C_{ijkl} may be replaced by T_p and C_{pq} , where the pairs of suffixes ij and kl have been replaced respectively by the suffixes p and q , running from one to six. In both cases, however, no factors of $\frac{1}{2}$ are necessary and the strain energy density may be expressed in the form

$$U = \int T_p dE_p = \int (C_{pq} E_q) dE_p = \frac{1}{2} C_{pq} E_p E_q. \quad \dots \quad (8)$$

The number of independent elastic constants occurring in this expression may be considerably reduced by the presence of crystal symmetry. Since the ferromagnetic metals all belong to crystal classes of high symmetry, many simplifying relations exist between the elastic coefficients (Love 1944). For a cubic crystal only twelve of the C_{pq} are non-zero and, of these, only three are independent, namely $C_{11} = C_{22} = C_{33}$, $C_{12} = C_{21} = C_{23} = C_{32} = C_{31} = C_{13}$ and $C_{44} = C_{55} = C_{66}$. If the symmetry of

the crystal is hexagonal, the same twelve coefficients are non-zero but the number of independent constants is increased to five, namely $C_{11}=C_{22}$, C_{33} , $C_{12}=C_{21}$, $C_{13}=C_{31}=C_{23}=C_{32}$ and $C_{44}=C_{55}$, where $C_{66}=\frac{1}{2}(C_{11}-C_{12})$. The experimentally determined values of the stiffness constants and compliance moduli of iron, cobalt and nickel have been collected in the table, the S_{pq} being defined by eqn. (14).

Experimental Values of the Elastic Coefficients

(The units are 10^{12} dyne cm^{-2} for C and 10^{-13} cm^2 dyne $^{-1}$ for S . The symbol 's' denotes a static measurement, 'd' a dynamic measurement and 'm' that the crystal was saturated magnetically).

C_{11}	C_{12}	C_{44}	S_{11}	S_{12}	S_{44}	Reference
IRON						
2.42	1.47	1.117	7.65	-2.89	8.95	Kimura and Ohno (1934)
2.28	1.33	1.109	7.72	-2.85	9.02	Kimura (1939)s
2.09	1.14	1.114	7.73	-2.72	8.98	Kimura (1939)d
2.37	1.41	1.160	7.57	-2.82	8.62	Goens and Schmid (1931)
NICKEL						
2.44	1.58	1.02	8.35	-3.28	9.8	Yamamoto (1950)
2.52	1.51	1.04	7.24	-2.72	9.56	Honda and Shirakawa (1949)
2.50	1.60	1.185	7.99	-3.12	8.44	Bozorth <i>et al.</i> (1949)
2.512	1.571	1.213	7.67	-2.95	8.24	Bozorth <i>et al.</i> (1951)
2.436	1.494	1.196	7.69	-2.92	8.36	de Klerk and Musgrave (1955)
2.526	1.561	1.226	7.50	-2.86	8.16	Bozorth <i>et al.</i> (1951)m
2.528	1.52	1.238	7.21	-2.71	8.08	Neighbours <i>et al.</i> (1952)m
2.465	1.473	1.247	7.34	-2.74	8.02	de Klerk and Musgrave (1955)m
COBALT						
C_{11}	C_{33}	C_{12}	C_{13}	C_{44}	Reference	
2.63	2.83	1.52	1.33	0.52	Honda and Shirakawa (1949) McSkimin <i>et al.</i> (1954)	
3.071	3.581	1.650	1.027	0.755		
S_{11}	S_{33}	S_{12}	S_{13}	S_{44}	Honda and Shirakawa (1949) McSkimin <i>et al.</i> (1954)	
6.22	5.08	-2.77	-1.63	19.3		
4.73	3.19	-2.31	-0.69	13.24		

2.2. *The Spontaneous Magnetostriction of Cubic Crystals*

Since the deformation of a crystal arising from the presence of the spontaneous magnetostriction is small, the dependence of the magnetic energy on the state of strain of the lattice may conveniently be introduced by expanding V as a Maclaurin series in the E_{ij} . Thus

$$V = V^0 + V_p{}^0 E_p + V_{pq}{}^0 E_p E_q + \dots, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where the association of the subscripts p, q, \dots with the symbol V indicates successive partial differentiation with respect to E_p, E_q, \dots in the order indicated by the subscripts. The zero superscript indicates that these quantities are to be evaluated at zero lattice strain and they can therefore be functions only of the direction of magnetization. The first term, V^0 , is thus a function of the α 's only and it is readily identified with the magnetic anisotropy energy measured at zero strain, that is for an undeformed crystal. The form of V^0 is dictated entirely by the requirements of crystal symmetry. For a cubic crystal, an application of the procedure outlined in § 1.2 results in the familiar expression

$$V^0 = K_0 + K_1 S(\alpha_1^2 \alpha_2^2) + K_2 (\alpha_1^2 \alpha_2^2 \alpha_3^2) \\ + K_3 S(\alpha_1^8) + K_4 S(\alpha_1^4 \alpha_2^4) + \dots, \quad (10)$$

the coefficients K_0, K_1, K_2, \dots being the anisotropy constants. The fourth and subsequent terms in this expression may usually be ignored. The term in K_2 is negligible for nickel and is often neglected for iron. The second term in eqn. (9), $V_p^0 E_p$, arises from the interaction between magnetic anisotropy and strain, and it may therefore be identified with the magnetostrictive energy. Again, the quantity V_p^0 can depend only upon the α 's. The third term $\frac{1}{2} V_{pq}^0 E_p E_q$ may be regarded as an additional contribution to the elastic energy $\frac{1}{2} C_{pq} E_p E_q$ which incorporates the effect upon the crystal symmetry of the deformation of the lattice. This arises because the distortion of the body due to the spontaneous magnetostriction results in the crystal lattice having a lower symmetry than the original undeformed crystal. Thus for a cubic crystal more than three elastic coefficients are involved and the term $\frac{1}{2} V_{pq}^0 E_p E_q$ introduces the required additional constants which are, of course, small compared with the C_{pq} . Effects of this type, which arise when elastic strains alter the symmetry of a structure, have been called morphic effects by Mueller (1940) and the corresponding energy is usually referred to as morphic energy.

The strain in the equilibrium state may now be found by minimizing $(U + V)$ with respect to all the strain components, i.e. with respect to all the E_p . Retaining only the first three terms in eqn. (9), that is neglecting powers of the strain components higher than the second, and setting the partial derivative of $(U + V)$ with respect to E_r equal to zero, yields the six minimal equations

$$C_{pr} E_p^v + V_r^0 + V_{pr}^0 E_p^v = 0. \quad (11)$$

It may be seen that the coefficients V_{pr}^0 of the morphic energy terms enter eqns. (11) only together with the elastic constants C_{pr} , as coefficients of the E_p^v . Since the C_{pr} do not, in general, all vanish for any of the minimal equations, V_{pr}^0 may be neglected in favour of C_{pr} and eqns. (11) become

$$V_r^0 = -C_{pr} E_p^v. \quad (12)$$

The elastic stiffness constants C_{pq} may, however, be regarded as components of a square matrix C whose reciprocal matrix $S = C^{-1}$ is composed of

coefficients S_{pq} which are the contracted (matrix) forms of the elastic compliance moduli S_{ijkl} . The solutions of eqn. (12) may then be written in the compact form

$$E_p{}^v = -S_{pr}V_r{}^0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where the equation $S = C^{-1}$ may be expressed in terms of the individual components by means of the relations

$$\begin{aligned} S_{pq}C_{qr} &= 1 & \text{for } p=r \\ \text{and } S_{pq}C_{qr} &= 0 & \text{for } p \neq r. \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

For a cubic crystal the existence of only three independent elastic moduli considerably simplifies eqns. (13) which become

$$\begin{aligned} E_p{}^v &= -(S_{11} - S_{12})V_p{}^0 - S_{12}(V_1{}^0 + V_2{}^0 + V_3{}^0) & \text{for } p=1, 2, 3 \\ \text{and } E_p{}^v &= -S_{44}V_p{}^0 & \text{for } p=4, 5, 6, \end{aligned} \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where it may be shown (Voigt 1928) that the relations (14) reduce to

$$\begin{aligned} S_{11} &= (C_{11} + C_{12})/(C_{11} - C_{12})(C_{11} + 2C_{12}), \\ S_{12} &= -C_{12}/(C_{11} - C_{12})(C_{11} + 2C_{12}), \quad S_{44} = 1/C_{44}. \end{aligned} \quad . \quad . \quad (16)$$

To proceed further in the evaluation of the lattice strain in the equilibrium state it is necessary to invoke considerations of symmetry to express the $V_p{}^0$ as functions of the α_i . Since the $V_p{}^0$ must have the same invariance to crystal symmetry operations as possessed by the corresponding E_p , the form of $V_p{}^0$ is fundamentally different for the two cases $p=1, 2, 3$ and $p=4, 5, 6$. Thus, $V_1{}^0$ must be independent of a change in sign of any of the α 's and of interchange of α_2 and α_3 . It must therefore be a function of α_1^2 and $\alpha_2^2\alpha_3^2$ only and may thus be written

$$V_1{}^0 = L_0 + L_1\alpha_1^2 + L_2\alpha_1^4 + L_3\alpha_2^2\alpha_3^2 + L_4\alpha_1^6 + L_5\alpha_1^2\alpha_2^2\alpha_3^2 + \dots, \quad (17a)$$

where the L 's are constants. However, $V_4{}^0$, which must change sign with α_2 or α_3 and be independent of the sign of α_1 , may be written

$$V_4{}^0 = \alpha_2\alpha_3(M_0 + M_1\alpha_1^2 + M_2\alpha_1^4 + M_3\alpha_2^2\alpha_3^2 + \dots). \quad (17b)$$

The remaining strain components are, of course, given by similar expansions involving the same L 's and M 's. These coefficients are the magneto-elastic coupling constants referred to in § 1.3. If these values of $V_p{}^0$ are inserted in eqns. (15) then solutions may be obtained for the six equilibrium strain components $E_p{}^v$ in terms of the α 's. The substitution of these $E_p{}^v$ in eqn. (3) yields an expression for the spontaneous lattice strain, λ , which is identical with eqn. (4) provided that

$$\begin{aligned} A_0 &= -L_0S_{11} - (2L_0 + L_1 + L_2 + L_4)S_{12}, \\ A_1 &= -(L_1 - L_3)(S_{11} - S_{12}), \quad A_2 = -M_0S_{44}, \\ A_3 &= -L_3S_{11} + (2L_2 + 3L_4)S_{12}, \quad A_4 = -(L_2 + L_3)(S_{11} - S_{12}), \\ A_5 &= -M_1S_{44}, \quad A_6 = -L_4(S_{11} - S_{12}), \quad A_7 = -M_3S_{44}, \\ A_8 &= -M_2S_{44}, \quad A_9 = -L_5S_{11} - (3L_4 + 2L_5)S_{12}. \end{aligned} \quad . \quad . \quad . \quad (18)$$

The first three of these relations may be compared with the work of Kittel (1949) who evaluated A_0 , A_1 and A_2 by assuming the simplest possible forms for eqns. (17), namely $V_1^0 = L_1\alpha_1^2$ and $V_4^0 = M_0\alpha_2\alpha_3$. It may be noted that the expression for A_0 derived above does not agree with that given by Kittel who obtained $A_0 = -3L_1S_{12}$. The expressions for A_1 and A_2 of eqns. (18) correspond, however, with the values obtained by Kittel, namely $A_1 = -L_1(S_{11} - S_{12})$ and $A_2 = -M_0S_{44}$.

2.3. The Spontaneous Magnetostriction of Hexagonal Crystals

The evaluation of an expression for the spontaneous magnetostriction of hexagonal crystals proceeds by the same method as that employed for cubic crystals but since the symmetry of hexagonal crystals is lower the situation is slightly more complicated. The coordinate axes x_1 , x_2 and x_3 may be assumed to coincide with the $[1\bar{2}0]$, $[10\cdot0]$ and $[00\cdot1]$ crystallographic axes and the expression for V^0 corresponding to equation (10) is then

$$V^0 = K_0 + K_1(\alpha_1^2 + \alpha_2^2) + K_2(\alpha_1^2 + \alpha_2^2)^2 + K_3(\alpha_1^2 + \alpha_2^2)^3 \\ + K_4(\alpha_1^2 - \alpha_2^2)(\alpha_1^4 - 8\alpha_1^2\alpha_2^2 + \alpha_2^4) + \dots \quad (19)$$

The fourth and subsequent terms are usually neglected so that (19) then corresponds to cylindrical rather than hexagonal symmetry. The equilibrium strain components, E_p^v , are again given by (13) and because of the existence of only five independent elastic moduli these equations may be written in the form

$$E_1^v = -S_{11}V_1^0 - S_{12}V_2^0 - S_{13}V_3^0, \\ E_2^v = -S_{12}V_1^0 - S_{11}V_2^0 - S_{13}V_3^0, \\ E_3^v = -S_{13}(V_1^0 + V_2^0) - S_{33}V_3^0, \\ E_4^v = -S_{44}V_4^0, \quad E_5^v = -S_{44}V_5^0, \\ E_6^v = -S_{66}V_6^0 = -2(S_{11} - S_{12})V_6^0, \quad (20)$$

where the relations (14) reduce, in this case, to the expressions

$$C_{11} + C_{12} = S_{33}/S, \quad C_{11} - C_{12} = 1/(S_{11} - S_{12}), \quad C_{13} = -S_{13}/S, \\ C_{33} = (S_{11} + S_{12})/S, \quad C_{44} = 1/S_{44}, \quad S = S_{33}(S_{11} + S_{12}) - 2S_{13}^2. \quad (21)$$

To express the quantities V_p^0 as functions of the α 's, eqns. (17) may be replaced by the following expansions

$$V_1^0 = L_0 + (L_1 - L_3)\alpha_1^2 + (L_2 - L_3)\alpha_2^2 + 8L_3\alpha_1^2\alpha_2^2 + (L_4 + L_3)\alpha_2^2\alpha_3^2 \\ + (L_5 + L_3)\alpha_3^2\alpha_1^2, \\ V_2^0 = L_0 + (L_1 + L_3)\alpha_2^2 + (L_2 + L_3)\alpha_1^2 - 8L_3\alpha_1^2\alpha_2^2 + (L_4 - L_3)\alpha_3^2\alpha_1^2 \\ + (L_5 - L_3)\alpha_2^2\alpha_3^2, \\ V_3^0 = M_0 + M_1(\alpha_1^2 + \alpha_2^2) + M_2(\alpha_1^2 + \alpha_2^2)\alpha_3^2, \\ V_4^0 = \alpha_2\alpha_3(N_0 + N_1\alpha_3^2), \quad V_5^0 = \alpha_3\alpha_1(N_0 + N_1\alpha_3^2), \\ V_6^0 = \alpha_1\alpha_2[(L_1 - L_2) - (L_4 - L_5)\alpha_3^2 + 4L_3(\alpha_1^2 - \alpha_2^2)]. \quad (22)$$

If these values of V_p^0 are inserted, as before, in eqns. (20) then the equilibrium strain components E_p^v may be readily obtained. The substitution of these E_p^v in eqn. (3) again yields an expression for the spontaneous lattice strain, which, after some manipulation, may be put in the form

$$\begin{aligned}\lambda = & Q_0 + Q_1\beta_3^2 \\ & + [Q_2 + Q_3\alpha_3^2](1 - \alpha_3^2) \\ & + [Q_4 + Q_5\alpha_3^2](1 - \alpha_3^2)\beta_3^2 \\ & + [Q_6 + Q_7\alpha_3^2](\alpha_1\beta_1 + \alpha_2\beta_2)\alpha_3\beta_3, \\ & + [Q_8 + Q_9\alpha_3^2](\alpha_1\beta_1 + \alpha_2\beta_2)^2 \\ & + Q_{10}(2\alpha_1\alpha_2\beta_1 + \alpha_1^2\beta_2 - \alpha_2^2\beta_2)^2. \quad . \quad . \quad . \quad . \quad (23)\end{aligned}$$

The magnetostriction constants $Q_0 \dots Q_{10}$ occurring in this equation are connected with the magneto-elastic coupling constants and the elastic compliance moduli by means of the relations

$$\begin{aligned}Q_0 = & -L_0(S_{11} + S_{12}) - M_0S_{13}, \\ Q_1 = & -L_0(2S_{13} - S_{11} - S_{12}) + M_0(S_{13} - S_{33}), \\ Q_2 = & -(L_1 + L_3)S_{12} - (L_2 - L_3)S_{11} - M_1S_{13}, \\ Q_3 = & -(L_4 + L_3)S_{12} - (L_2 - L_3)S_{11} - M_1S_{13}, \\ Q_4 = & -(L_1 + L_2)S_{13} + (L_1 + L_3)S_{12} \\ & + (L_2 - L_3)S_{11} + M_1(S_{13} - S_{33}), \\ Q_5 = & -(L_4 + L_5)S_{13} + (L_4 + L_3)S_{11} \\ & + (L_5 - L_3)S_{12} + M_2(S_{13} - S_{33}), \\ Q_6 = & -N_0S_{44}, \quad Q_7 = -N_1S_{44}, \\ Q_8 = & -(L_1 - L_2)(S_{11} - S_{12}), \\ Q_9 = & -(L_5 - L_4)(S_{11} - S_{12}), \\ Q_{10} = & -2L_3(S_{11} - S_{12}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)\end{aligned}$$

The occurrence of the coefficient Q_1 emphasizes the observation made in § 1.3 that for non-cubic crystals the expression for the spontaneous magnetostriction may contain isotropic-anisotropic terms.

It is of some interest to note that the expression for the spontaneous magnetostriction given by eqn. (23) contains only one term—that multiplied by Q_{10} —which is characteristic of hexagonal symmetry. If the last term is omitted from this expression, the spontaneous magnetostriction conforms to cylindrical symmetry. This may be seen by expressing λ in terms of the angles α and β made by the directions α and β with the hexagonal axis, and the angle γ between the two planes each containing one of these directions and the hexagonal axis, as shown in fig. 1. It then follows from the relations

$$\begin{aligned}\alpha_3 = & \cos \alpha, \quad \beta_3 = \cos \beta, \\ (\alpha_1\beta_1 + \alpha_2\beta_2) = & \sin \alpha \sin \beta \cos \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)\end{aligned}$$

that the modified expression for λ is independent of the orientation of both α and β with respect to the non-hexagonal axes.

2.4. The Form Effect in Single Crystals

If it is remembered that U , V and W were defined in § 2.1 as energy densities relative to the undeformed crystal, of volume τ^0 , rather than relative to the deformed crystal, of volume $\tau = \tau^0(1 + \omega)$, then it may be seen that the demagnetizing energy density, W , is given by

$$W\tau^0 = \frac{1}{2} I_8^2 D_{ij} \alpha_i \alpha_j \tau, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Fig. 1

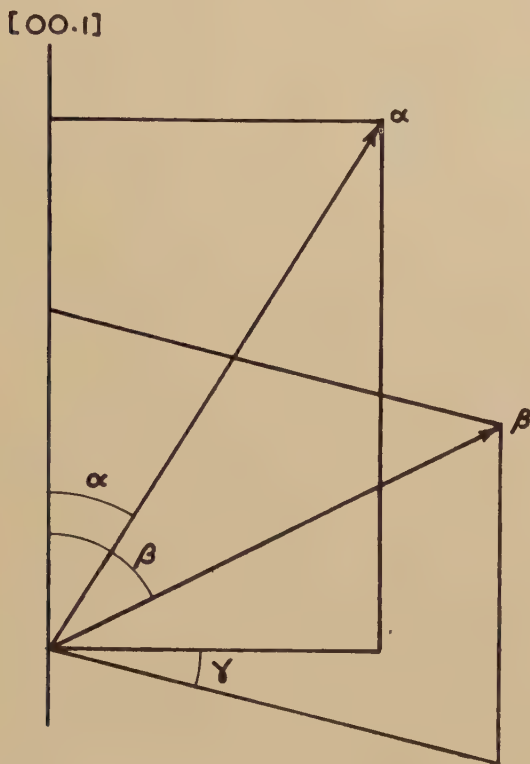


Diagram showing the angles occurring in eqns. (25).

where the demagnetizing coefficients, D_{ij} , connect the components, $(H - X)_i = D_{ij} I_{s\alpha_j}$, of the demagnetizing field with the components, $I_{s\alpha_j}$, of the bulk magnetization. The equilibrium components of strain, E_{ij}^w , may be found by minimizing the quantity $(U + W)$ with respect to changes in the E_{ij} , the minimal equations corresponding to (11) being

$$C_{klmn}E_{kl}^w + \frac{\partial \omega}{\partial E_{mn}} (\frac{1}{2} I_s^0 D_{ij}^0 \alpha_i \alpha_j) + \frac{\partial I_s}{\partial E_{mn}} (I_s^0 D_{ij}^0 \alpha_i \alpha_j) + \frac{\partial D_{ij}}{\partial E_{mn}} \alpha_i \alpha_j (\frac{1}{2} I_s^0) = 0, \quad (27)$$

where the zero superscript indicates that the quantities are to be evaluated at equilibrium. The equilibrium components of strain may therefore be written in the form

$$E_{kl}^w = (E_{kl}^w)_1 + (E_{kl}^w)_2 + (E_{kl}^w)_3, \quad . \quad . \quad . \quad . \quad . \quad (28)$$

where

$$(E_{kl}^w)_1 = -S_{klmn} \frac{\partial \omega}{\partial E_{mn}} (\frac{1}{2} I_s^0 D_{ij}^0 \alpha_i \alpha_j), \quad . \quad . \quad . \quad (29a)$$

$$(E_{kl}^w)_2 = -S_{klmn} \frac{\partial I_s}{\partial E_{mn}} (I_s^0 D_{ij}^0 \alpha_i \alpha_j), \quad . \quad . \quad . \quad (29b)$$

$$(E_{kl}^w)_3 = -S_{klmn} \frac{\partial D_{ij}}{\partial E_{mn}} \alpha_i \alpha_j (\frac{1}{2} I_s^0) \quad . \quad . \quad . \quad . \quad (29c)$$

and the S_{klmn} are the uncontracted (tensor) forms of the elastic compliance moduli, S_{pq} . It then follows from eqn. (3) that the correction to the spontaneous magnetostriction due to the form effect is given by

$$\Delta\lambda = (\Delta\lambda)_1 + (\Delta\lambda)_2 + (\Delta\lambda)_3, \quad . \quad . \quad . \quad . \quad (30)$$

where $(\Delta\lambda)_i = (E_{kl}^w)_i \beta_k \beta_l$. The evaluation of these three components of $\Delta\lambda$ proceeds as follows.

For a given direction of magnetization, that is for fixed values of the α_i , the component $(\Delta\lambda)_1$ may be evaluated immediately from

$$(\Delta\lambda)_1 = (-\frac{1}{2} I_s^0 D_{ij}^0 \alpha_i \alpha_j) S_{klmn} \frac{\partial \omega}{\partial E_{mn}} \beta_k \beta_l \quad . \quad . \quad . \quad (31)$$

by substituting $(E_{11} + E_{22} + E_{33})$ for ω . The form of $(\Delta\lambda)_1$ depends upon the symmetry of the crystal: for cubic crystals

$$(\Delta\lambda)_1 = (-\frac{1}{2} I_s^0 D_{ij}^0 \alpha_i \alpha_j) (S_{11} + 2S_{12}) \quad . \quad . \quad . \quad (32a)$$

whilst for hexagonal crystals

$$(\Delta\lambda)_1 = (-\frac{1}{2} I_s^0 D_{ij}^0 \alpha_i \alpha_j) [(S_{11} + S_{12} + S_{13}) + (S_{13} + S_{33} - S_{11} - S_{12}) \beta_3^2]. \quad . \quad . \quad . \quad (32b)$$

The component $(\Delta\lambda)_2$ cannot be evaluated immediately because of the occurrence of the unknown factors $\partial I_s / \partial E_{mn}$. It is possible, however, to express $(\Delta\lambda)_2$ in terms of $(\Delta\lambda)_1$ and the forced magnetostriction constants P_i' of eqn. (5) by using the thermodynamic relations.

$$\tau^0 \frac{\partial E_{kl}}{\partial H} = \frac{\partial (\tau I_s)}{\partial T_{kl}}, \quad . \quad . \quad . \quad . \quad (33)$$

together with the transformations

$$\frac{\partial}{\partial T_{kl}} = S_{klmn} \frac{\partial}{\partial E_{mn}}. \quad . \quad . \quad . \quad . \quad (34)$$

These permit the quantities $S_{klmn} (\partial I_s / \partial E_{mn})$ to be written in the form

$$S_{klmn} \frac{\partial I_s}{\partial E_{mn}} = \frac{\partial E_{kl}}{\partial H} - \frac{I_s^0}{\tau^0} \frac{\partial \tau}{\partial T_{kl}} = \frac{\partial E_{kl}}{\partial H} - I_s^0 S_{klmn} \frac{\partial \omega}{\partial E_{mn}}. \quad . \quad (35)$$

If eqn. (3) is compared with eqn. (5) then it may be observed that

$$\frac{\partial E_{kl}}{\partial H} \beta_k \beta_l = \frac{\partial}{\partial H} (\lambda + \Delta\lambda) = (P'_i)_a S_i \quad . \quad . \quad . \quad (36)$$

and it is therefore possible to express $(\Delta\lambda)_2$ in terms of $(\Delta\lambda)_1$ and the known functions S_i occurring in the expression for the spontaneous magnetostriction. Thus

$$(\Delta\lambda)_2 = -I_s^0 D_{ij}^0 \alpha_i \alpha_j (P'_k)_a S_k - 2(\Delta\lambda)_1. \quad . \quad . \quad . \quad (37)$$

Evaluation of $(\Delta\lambda)_3$ demands a determination of the strain dependence of the demagnetizing coefficients, i.e. of the quantities $D'_{ijkl} = \partial D_{ij} / \partial E_{kl}$. For the general case of an ellipsoid the calculation of the D'_{ijkl} presents some difficulty. Usually, however, it is quite sufficient to deal with the degenerate cases of prolate and oblate spheroids and for crystals of these shapes most of the calculation required has been performed by Powell (1931). If the position of a point in the body is defined by the coordinates x relative to the principal axes of the spheroid and x_i (as before) relative to the (orthogonal) axes of the crystal, then

$$x = l_{ij} x_j, \quad x_i = l_{ji} x, \quad . \quad . \quad . \quad . \quad (38)$$

where l_{ij} is the direction cosine of the axis x with respect to the axis x_j . Referred to the x axes, only three of the demagnetizing coefficients are non-zero, namely, $_{11}D$, $_{22}D$ and $_{33}D$. The corresponding non-zero derivatives have been calculated by Powell. For an oblate spheroid they are

$$\begin{aligned} _{1111}D' &= (3\pi/2e^4)[(1-e^2)(3+2e^2) - \frac{3}{2}\sqrt{(1-e^2)}\sin^{-1}e], \\ _{1122}D' &= (4/e^2)(1-e^2)_{11}D - (\pi/2e^4)(1-e^2)(14e^2+13) \\ &\quad + (\pi/2e^5)(8e^2+17)\sqrt{(1-e^2)}\sin^{-1}e, \\ _{1133}D' &= -(4/e^2)(1-e^2)_{11}D + (4\pi/e^5)(1-e^2) \\ &\quad \times [2e^3+e-(e^2+1)/(1-e^2)\sin^{-1}e], \quad . \quad . \quad . \quad (39) \end{aligned}$$

where e is the eccentricity of the spheroid. For a prolate spheroid $(1-e^2)$ must be replaced by $1/(1-e^2)$ in (39). If the corresponding values of the D'_{ijkl} —obtained by use of the transformations (38)—are substituted in eqn. (29c), an expression is obtained for $(\Delta\lambda)_3$ which may be written in the general form

$$(\Delta\lambda)_3 = -S_{klmn} \mu^0_{ijmn} \alpha_i \alpha_j \beta_k \beta_l, \quad . \quad . \quad . \quad (40)$$

where

$$\mu^0_{ijmn} = \frac{1}{2} I_s^0 D'_{ijmn} = \frac{1}{2} I_s^0 \frac{\partial D_{ij}}{\partial E_{mn}}. \quad . \quad . \quad . \quad (41)$$

The evaluation of $(\Delta\lambda)_3$ is, in general, laborious but for special symmetrical orientations of the crystal it may be calculated without undue difficulty. For cubic crystals the form of eqn. (40) is such that $(\Delta\lambda)_3$ may be expressed as small corrections, ΔA_1 and ΔA_2 , to the spontaneous magnetostriction constants A_1 and A_2 . For example, if the magnetization is confined to the equatorial plane of an oblate spheroid, and if this plane contains the [001] axis, then

$$\Delta A_1 = -(S_{11} - S_{12})\mu, \quad \Delta A_2 = -S_{44}\mu, \quad . \quad . \quad . \quad (42a)$$

where the quantity μ is given by the expression

$$\mu = (\pi I_s^0 / 2e^5) [(1-e^2)(3e+2e^2) - 3\sqrt{(1-e^2)}\sin^{-1}e]. \quad . \quad (42b)$$

For a prolate spheroid, replacing $(1-e^2)$ by $1/(1-e^2)$,

$$\mu = (\pi I_s^0 / 4e^5) [(6e-10e^3) - 3(1-e^2)^2 \ln(1+e)/(1-e)]. \quad . \quad (42c)$$

The specimens employed for accurate evaluations of the spontaneous magnetostriction constants are usually in the form of very thin disc-shaped crystals for which the D_{ijkl} are small. Since $e \simeq 1$, μ is also usually small and even when the materials investigated are those with the highest values of I_s —the ferromagnetic metals—the strain introduced by the form effect is considerably less than 10^{-6} for thin specimens. When the magnetostriction constants are large compared with 10^{-6} , as in nickel and cobalt, the form effect is always neglected (Bozorth 1954). If, however, one or more of the spontaneous magnetostriction constants is small, as in iron (Carr 1950), the iron-silicon alloys (Carr and Smoluchowski 1951) and the iron-aluminium alloys (Hall 1957), the contribution of the form effect may be significant. In both these alloy systems the magnetostriction is a function of the composition of the alloy and the importance of the form effect is associated primarily with a change in sign of A_1 and A_2 . In such circumstances, and especially when thick disc-shaped specimens are employed, the contribution of the form effect to the magnetostriction should not be neglected.

2.5. Comparison with Experiment: the Demagnetized State

The most complete investigation of the magnetostrictive behaviour of single crystals of cubic ferromagnetic materials is that carried out by Masiyama (1928) who used three flat spheroids of nickel and measured the magnetostriction in various directions in the (100), (110) and (111) planes. The results obtained were subsequently used by Becker and Döring (1939) and Mason (1951) to evaluate the saturation magnetostriction constants of nickel. As a result of the work of Becker and Döring, it has been generally supposed (Bozorth 1951, Stewart 1954, Vautier 1954) that the expression for the spontaneous magnetostriction λ must contain terms of at least sixth order in the α 's to account for the observed magnetostriction in the (111) plane. In addition, Mason claimed that such terms were necessary to explain the observed behaviour in the (110) plane. More recent work (Birss 1957) has shown, however, that both suppositions are founded upon a misinterpretation of Masiyama's original results. It is now considered that the experimental data at present available are completely consistent with an equation of the form

$$\begin{aligned} \lambda = & B_0 + B_1 S(\alpha_1^2 \beta_1^2) + B_2 S(\alpha_1 \alpha_2 \beta_1 \beta_2) + B_3 S(\alpha_1^2 \alpha_2^2) \\ & + B_4 S(\alpha_1^4 \beta_1^2) + B_5 S(\alpha_1 \alpha_2 \alpha_3^2 \beta_1 \beta_2). \quad . \quad . \quad . \quad . \quad (43) \end{aligned}$$

Most of the early investigations of ferromagnetic magnetostriction, including that mentioned above, suffered from a common disadvantage in that all measurements of changes in length were referred to an initial demagnetized state. This is an unsatisfactory reference state, since the associated distribution of domains in the crystal may depend upon the method of demagnetization. Thus the demagnetized state may not correspond to a unique reference state common to all the specimens used

in these investigations. Furthermore, the method of demagnetization may not, in general, be standardized, since for specimens of different shapes the energy relations governing the demagnetization process will be different. The demagnetized state is moreover a state to which the equation $\lambda = P_i S_i$ may not readily be applied, so that the saturation magnetostriction constants may only be determined indirectly from such measurements. The procedure involved in such a determination consists in calculating the magnetostriction in the initial state in the manner outlined below.

When an unmagnetized crystal is magnetized to saturation, the resulting deformation of the crystal may be predicted from $\lambda = P_i S_i$ provided that the lattice strain in the demagnetized state can be evaluated. Since the actual distribution of domains in the demagnetized state is unknown, it is customary to consider only the ideal demagnetized state in which the crystal is composed of many domains, orientated so that there are equal numbers in each of the crystallographically equivalent directions of easy magnetization. The evaluation of the corresponding magnetostrictive strain, λ_i , leads to an expression for $\Lambda = \lambda - \lambda_i$ as a function of the directions α and β which refer, as before, to the saturated crystal. Λ thus represents the fractional change in length between the ideal demagnetized state and one of magnetic saturation in the direction α . When, for cubic crystals, the directions α and β are both parallel to a quaternary or a ternary axis, Λ is commonly denoted by λ_{100} or λ_{111} respectively.

The value of λ_i depends upon which crystallographic axes are directions of easy magnetization for a particular material. For example, if the easy directions are the quaternary axes, as in iron, then for domains aligned parallel or anti-parallel to the [100] direction, the strain in the direction β is $(B_0 + B_1\beta_1^2 + B_4\beta_1^2)$. For the [010] and [001] directions β_1^2 is replaced by β_2^2 and β_3^2 respectively. If the customary assumption is made that the magnetostrictive strains of the individual domains may be added together algebraically after multiplication by suitable weighting factors proportional to their volumes, then

$$\lambda_i = B_0 + \frac{1}{3}B_1 + \frac{1}{3}B_4. \quad . \quad . \quad . \quad . \quad . \quad (44a)$$

Similarly if the directions of easy magnetization are the ternary axes, as in nickel, then

$$\lambda_i = B_0 + \frac{1}{3}B_1 + \frac{1}{3}B_3 + \frac{1}{9}B_4. \quad . \quad . \quad . \quad . \quad . \quad (44b)$$

The magnetostrictive strain associated with magnetization to saturation from the ideal demagnetized state may thus be found by combining eqns. (43) and (44). The resulting expression for $\Lambda = \lambda - \lambda_i$ contains two terms which both assume different forms for iron from those for nickel. One of the alternative forms may, however, be removed by incorporating the quantity $s = S(\alpha_1^2\alpha_2^2)$ into one of the terms so that

$$\begin{aligned} \Lambda = & B_1[S(\alpha_1^2\beta_1^2) - \frac{1}{3}] + B_2S(\alpha_1\alpha_2\beta_1\beta_2) \\ & + B_3^*s \text{ for Fe or } + B_3^*(s - \frac{1}{3}) \text{ for Ni} \\ & + B_4[S(\alpha_1^4\beta_1^2) + \frac{2}{3}s - \frac{1}{3}] + B_5S(\alpha_1\alpha_2\alpha_3^2\beta_1\beta_2), \quad . \quad . \quad (45) \end{aligned}$$

where $B_3^* = B_3 - \frac{2}{3}B_4$. This equation is usually quoted in the form given by Becker and Döring (1939) in which the constants B_1, B_2, B_3^*, B_4 and B_5 are replaced by $h_1, 2h_2, h_3, h_4$ and $2h_5$ respectively. For hexagonal materials, such as cobalt, for which the easy directions are parallel and antiparallel to the $[00\cdot1]$ hexagonal axis

$$\lambda_i = Q_0 + Q_1\beta_3^2, \quad . \quad . \quad . \quad . \quad . \quad (46a)$$

and Λ may be obtained by omitting these two terms from the expression for λ given by (23). If the basal plane is a plane of easy magnetization

$$\lambda_i = Q_0 + Q_1\beta_3^2 + Q_2 + Q_4\beta_3^2 + \frac{1}{2}(Q_8 + Q_{10})(1 - \beta_3^2), \quad . \quad . \quad . \quad (46b)$$

and Λ may be obtained by subtracting this expression for λ_i from that for λ given by (23).

For many years the necessity of evaluating the saturation magnetostriction constants without reference to the initial demagnetized state was not generally realized and most of the reliable determinations of these constants are therefore of very recent origin. These determinations are discussed in § 2.6 where the possibility of employing equations of lower order is investigated. It is, however, convenient to quote at this point the standard expressions for the spontaneous magnetostriction carried to lower approximations than that involving fourth powers of the α 's. For cubic crystals, the second-order equation is the same as the three leading terms of eqn. (4) but the coefficients again have a different significance so that

$$\lambda = C_0 + C_1S(\alpha_1^2\beta_1^2) + C_2S(\alpha_1\alpha_2\beta_1\beta_2), \quad . \quad . \quad . \quad . \quad (47)$$

This is the simplest equation consistent with anisotropic magnetostriction and is often written in the alternative form

$$\Lambda = \frac{2}{3}\lambda_{100}[S(\alpha_1^2\beta_1^2) - \frac{1}{3}] + 3\lambda_{111}S(\alpha_1\alpha_2\beta_1\beta_2), \quad . \quad . \quad . \quad (48)$$

since, to this approximation, $\lambda_{100} = \frac{2}{3}C_1$ and $\lambda_{111} = \frac{1}{3}C_2$. If the additional simplifying limitation is imposed that $\lambda_{100} = \lambda_{111}$ ($=\lambda_s$ say), then eqns. (47) and (48) reduce to

$$\lambda = C_0 + \frac{2}{3}\lambda_s \cos^2 x \quad . \quad . \quad . \quad . \quad . \quad (49)$$

and

$$\Lambda = \frac{2}{3}\lambda_s (\cos^2 x - \frac{1}{3}), \quad . \quad . \quad . \quad . \quad . \quad (50)$$

where $\cos x = S(\alpha_1\beta_1)$ is the cosine of the angle between the directions α and β . This expression, which is commonly used to represent the behaviour of polycrystalline material at saturation, contains no reference to the crystal axes and therefore represents isotropic magnetostriction.

For hexagonal materials the second-order form of eqn. (23) corresponding to (47) may be obtained by setting $\alpha_3^2 = 0$ within the four sets of square brackets in (23). This procedure leads to an expression which conforms to cylindrical symmetry and which may be written in the form

$$\begin{aligned} \lambda = & R_0 + R_1\beta_3^2 + (R_2 + R_3\beta_3^2)(1 - \alpha_3^2) \\ & + [R_4\alpha_3\beta_3 + R_5(\alpha_1\beta_1 + \alpha_2\beta_2)](\alpha_1\beta_1 + \alpha_2\beta_2), \quad . \quad . \quad (51) \end{aligned}$$

where, as before, the subscripts 1, 2, 3 refer respectively to the $[1\bar{2}0]$, $[10\cdot0]$ and $[00\cdot1]$ crystallographic axes. In terms of the angles of fig. 1,

$$\begin{aligned}\lambda = & R_0 + R_1 \cos^2 \beta + (R_2 + R_3 \cos^2 \beta) \sin^2 \alpha \\ & + \frac{1}{4} R_4 \sin 2\alpha \sin 2\beta \cos \gamma \\ & + R_5 \sin^2 \alpha \sin^2 \beta \cos^2 \gamma. \quad . \quad . \quad . \quad . \quad . \quad (52)\end{aligned}$$

The corresponding equations for Λ may be readily obtained from these equations and from expressions for λ_i corresponding to (46) which are respectively

$$\lambda_i = R_0 + R_1 \beta_3^2 \quad . \quad . \quad . \quad . \quad . \quad (53a)$$

and
$$\lambda_i = R_0 + R_1 \beta_3^2 + R_2 + R_3 \beta_3^2 + \frac{1}{2} R_5 (1 - \beta_3^2). \quad . \quad . \quad . \quad . \quad (53b)$$

In both cases examination of the form of Λ shows that it is not possible, by a suitable selection of finite values for the constants $R_2 \dots R_5$, to reduce Λ to the form (50) or to the more general form

$$\Lambda = \xi + \eta \cos^2 x. \quad . \quad . \quad . \quad . \quad . \quad (54)$$

2.6. Evaluation of the Saturation Magnetostriction Constants

Since the ideal demagnetized state very rarely exists in actual ferromagnetic crystals (Lee 1955*b*), it is not possible to use an expression for Λ to determine the magnetostriction constants directly. The equation $\lambda = P_i S_i$ predicts the spontaneous magnetostriction referred to an experimentally inaccessible state, and hence the magnetostriction constants must be determined by measurements at saturation. Thus the direction of measurement must be fixed and the variation of λ for different directions of the magnetization vector measured. In this way the isotropic-isotropic and isotropic-anisotropic saturation magnetostriction constants are eliminated but the remaining anisotropic-isotropic and anisotropic-anisotropic constants may be determined. For simplicity of experimental arrangement and interpretation of results the various directions of magnetization should preferably be coplanar. The direction α is thus characterized by a single azimuthal angle whereas the direction β may conveniently be taken to lie either in the plane or normal to it. The mathematical interpretation of the results is greatly facilitated if the plane is one of the principal crystallographic planes, e.g. a plane of the type (100), (110) or (111).

The arrangement with β normal to the plane of magnetization has been used by Kaya (1928) to investigate the saturation magnetoresistance of a single crystal of nickel, the magnetoresistive behaviour of cubic crystals being, by entirely analogous symmetry arguments, described by an equation of the same form as (4). No measurements of magnetostriction have, however, been made in this fashion; modern practice employs a flat disc-shaped specimen approximating to an oblate spheroid with the equatorial plane coinciding with a principal crystallographic plane. The crystal may thus be uniformly magnetized by a uniform magnetic field applied in this plane, as indicated in § 1.1.

For the cubic ferromagnetic metals, iron and nickel, the most accurate determination of the saturation magnetostriction constants is that due to Bozorth and Hamming (1953) who evaluated $B_1 \dots B_5$ for nickel and also for a 78% nickel-iron alloy. The values obtained for nickel, together with their estimated probable errors, are

$$\begin{aligned} B_1 &= (-68.8 \pm 3.8) \times 10^{-6}, & B_2 &= (-73.0 \pm 3.8) \times 10^{-6}, \\ B_3 &= (-7.8 \pm 4.5) \times 10^{-6}, & B_4 &= (-7.5 \pm 5.2) \times 10^{-6}, \\ B_5 &= (+15.4 \pm 6.2) \times 10^{-6}, & & \dots \dots \dots (55) \end{aligned}$$

and Bozorth and Hamming concluded that the values of the constants B_3 , B_4 and B_5 are "not certainly different from zero". The magnetostriction of iron and iron-silicon alloys has been investigated by various workers and a number of sets of experimental data have been correlated by Carr and Smoluchowski (1951) who concluded that the saturation magnetostriction of iron and iron-silicon alloys can be adequately described by an expression involving only two constants, e.g. eqn. (47). For pure iron these constants have the numerical values (Lee 1955a)

$$C_1 = +31.1 \times 10^{-6}, \quad C_2 = -63.6 \times 10^{-6}. \quad \dots \dots \dots (56)$$

The remaining two common ferromagnetic metals, cobalt and gadolinium, are both hexagonal at ordinary temperatures. The saturation magnetostriction constants of gadolinium have not yet been measured, presumably because of the difficulty of obtaining single crystal specimens. For cobalt the recent work of Bozorth and Sherwood (1954) and Bozorth (1954) has shown that the second-order equation (51) is a good representation of their experimental data, the measured values of the constants being

$$\begin{aligned} R_2 &= -95 \times 10^{-6}, & R_3 &= +205 \times 10^{-6}, \\ R_4 &= -465 \times 10^{-6}, & R_5 &= +50 \times 10^{-6}. & \dots \dots \dots (57) \end{aligned}$$

It may therefore be concluded that the magnetostrictive behaviour of the common ferromagnetic materials may be adequately represented by the second-order expressions (47) or (51) and that the inclusion of terms of a higher order is unnecessary.

For cubic crystals, the saturation magnetostriction constants C_1 and C_2 , occurring in eqn. (47), may be evaluated from measurements in the three principal planes as follows. Let the planes be, for convenience, the (001), (1 $\bar{1}$ 0) and (1 $\bar{1}$ 1) planes and let the measuring direction make an azimuthal angle β with the [110] direction. (The sense of β is such that the position $\beta = +90^\circ$ defines the axes [$\bar{1}$ 10], [001] and [$\bar{1}$ 12] respectively as shown in figs. 2(a), (b) and (c).) A rotation of the saturation magnetization vector from the direction β to the direction $\alpha = \beta + x$ is accompanied by a strain in the direction β which may be evaluated as a function of x , for various values of β . This quantity may be designated by $\lambda_x - \lambda_0$, where the suffix indicates the angle between the magnetization vector and the measuring direction. For all three principal planes it may be written in the form

$$\lambda_x - \lambda_0 = q(\cos 2x - 1) + 2r \sin 2\beta \sin 2x, \quad \dots \dots \dots (58)$$

where the functions $q = q(\beta)$ and $r = r(\beta)$, which depend only upon C_1 , C_2 and β , may be found from the equations

$$\begin{array}{ll} (001) & 8q = (2C_1 + C_2) - (2C_1 - C_2) \cos 4\beta, \\ \text{plane} & 8r = (2C_1 - C_2) \cos 2\beta, \end{array} \quad (59a)$$

$$\begin{array}{ll} (1\bar{1}0) & 32q = (6C_1 + 5C_2) - (2C_1 - C_2)(2 \cos 2\beta - 3 \cos 4\beta), \\ \text{plane} & 32r = (2C_1 - C_2)(1 - 3 \cos 2\beta), \end{array} \quad (59b)$$

$$\begin{array}{ll} (1\bar{1}1) & 6q = (C_1 + C_2), \quad r = 0. \\ \text{plane} & \end{array} \quad (59c)$$

Fig. 2

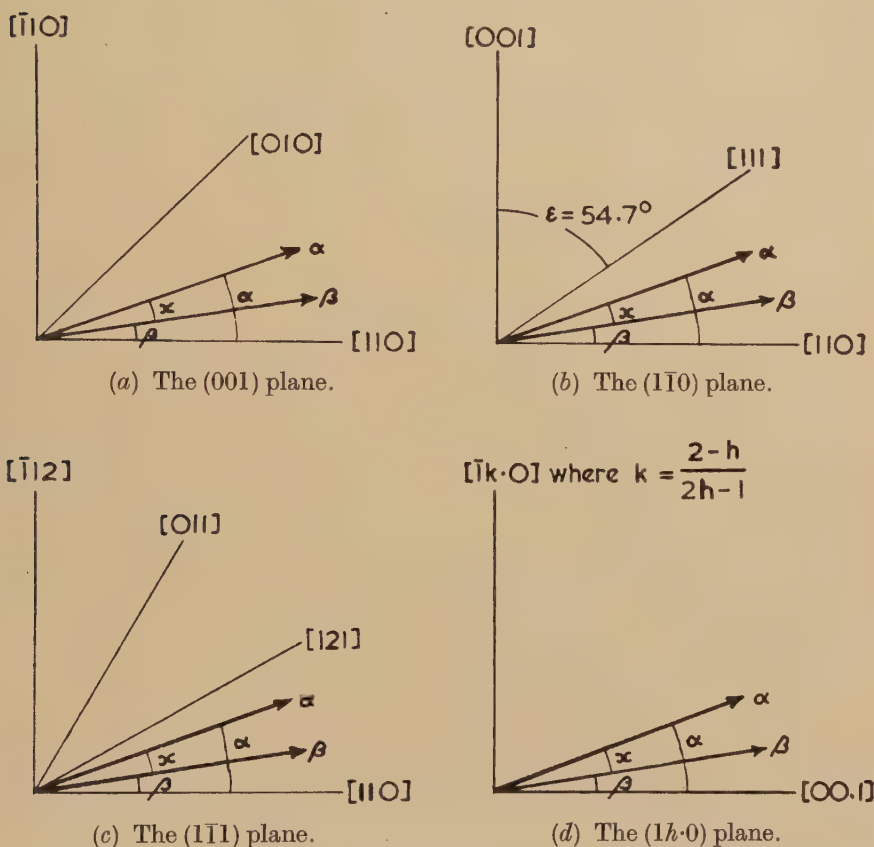


Diagram showing the angles associated with magnetization in various crystallographic planes and with eqns. (59).

These expressions may thus be employed to determine the values of C_1 and C_2 which correspond to the best agreement between the experimental data and the values obtained from eqn. (58). It may be noted at this point that (58) predicts the occurrence of alternate maxima and minima of $\lambda_x - \lambda_0$ at positions $x = \frac{1}{2} \tan^{-1} [(2r \sin 2\beta)/q]$ which are separated by intervals of 90° . It therefore follows that such an extremum position will coincide with the

direction of measurement only if $r \sin 2\beta = 0$. This condition is always satisfied in the (111) plane since $r=0$. In the (001) and (110) planes, however, an extremum will coincide with the measuring direction only if the latter is one of the principal crystallographic directions lying in the plane of the specimen.

If (58) is regarded as being an exact equation for the quantity $\lambda_x - \lambda_0$ rather than an approximation, then a pair of measurements suffices to determine C_1 and C_2 . For example, in the (001) plane, if $\beta = 0$ and $x = 90^\circ$ then $\lambda_x - \lambda_0 = -\frac{1}{2}C_2$, whilst if $\beta = 45^\circ$ and $x = 90^\circ$ then $\lambda_x - \lambda_0 = -C_1$. These values are often quoted as $-\frac{3}{2}\lambda_{111}$ and $-\frac{3}{2}\lambda_{100}$ respectively, but this practice is to be deprecated since it gives no indication of the order assumed for the magnetostriction equation. For example, if the fourth-order eqn. (43) is employed to correlate observations in the (001) plane, then B_5 (and hence λ_{111}) cannot be determined since α_3 vanishes for all directions in this plane. Furthermore, the procedure outlined above for determining C_1 now yields the value $\lambda_x - \lambda_0 = -B_1$ which is not equal to $-\frac{3}{2}\lambda_{100}$. To this approximation, for iron

$$\begin{aligned}\lambda_{100} &= \frac{2}{3}B_1 + \frac{2}{3}B_4, \\ \lambda_{111} &= \frac{1}{3}B_2 + \frac{1}{3}B_3 - \frac{2}{9}B_4 + \frac{1}{9}B_5 \quad . \quad . \quad . \quad . \quad (60 a)\end{aligned}$$

and for nickel

$$\begin{aligned}\lambda_{100} &= \frac{2}{3}B_1 - \frac{1}{3}B_3 + \frac{8}{9}B_4, \\ \lambda_{111} &= \frac{1}{3}B_2 + \frac{1}{9}B_5. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (60 b)\end{aligned}$$

For a hexagonal crystal, the constants R_2 , R_3 , R_4 and R_5 occurring in the expression (51) may all be determined by observations in any plane containing the [00.1] hexagonal axis. Since the second-order equation conforms to cylindrical symmetry, it is immaterial what orientation this plane possesses with respect to the other crystal axes. In the basal plane $\lambda_x - \lambda_0$ vanishes identically for the same reason. If β is now the angle between the measuring direction and the hexagonal axis (fig. 2(d)) then $\lambda_x - \lambda_0$ is again given by eqn. (58) together with the relations

$$\begin{aligned}8q &= (R_4 + R_5 - R_3) - (4R_2 + 2R_3 + 2R_5) \cos 2\beta - (R_3 + R_4 - R_5) \cos 4\beta, \\ 8r &= (2R_2 + R_3 + R_5) + (R_3 + R_4 - R_5) \cos 2\beta. \quad . \quad . \quad . \quad . \quad . \quad (59 d)\end{aligned}$$

As before, the most satisfactory method of evaluating the magnetostriction constants is by adjusting the values of q and r to obtain the best agreement with the experimental observations. If the measuring direction is parallel to the hexagonal axis ($\beta = 0$), then

$$\lambda_x - \lambda_0 = \frac{1}{2}(R_2 + R_3)(1 - \cos 2x) \quad . \quad . \quad . \quad . \quad . \quad (61)$$

and only two of the saturation magnetostriction constants are involved.

When it is necessary to employ the fourth-order eqns. (43) or (23) to describe the magnetostrictive behaviour of a given material (e.g. 30% Co-Fe, Goldman 1950), then the corresponding saturation magnetostriction constants may be evaluated in a similar manner to that outlined

above. Details of the method of such determinations have been given for cubic crystals by Bozorth and Hamming (1953) and for hexagonal crystals by Mason (1954).

§ 3. THE MAGNETOSTRICTION OF POLYCRYSTALS

3.1. Introduction

Since a polycrystalline substance is, ideally, an aggregate of a large number of individual crystallites orientated at random, it is possible, in principle, to relate the magnetostriction of a polycrystal to that of a single crystal specimen of the same material. In general, the mean magnetization in each crystal grain is influenced by that of its neighbours, but above the point of technical saturation a suitably shaped polycrystalline specimen may be uniformly magnetized by a uniform applied magnetic field. However, even at saturation the magnetostriction of a polycrystal may not necessarily be obtained by averaging, over all the relevant crystallographic directions, the magnetostrictive strain corresponding to a single crystal.

Fig. 3

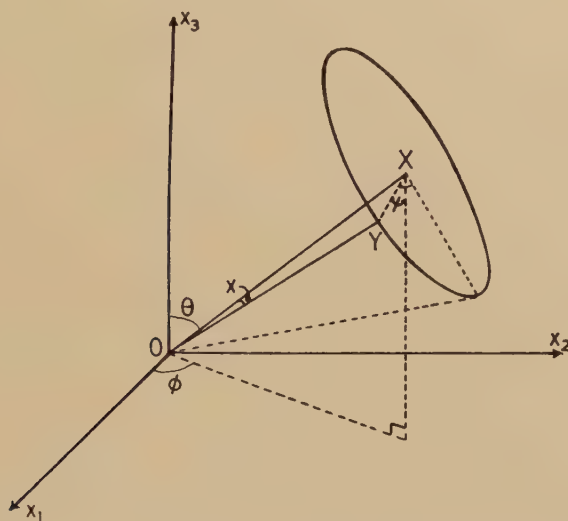


Diagram showing the angles occurring in eqns. (62) and (63).

It has been pointed out by Vladimírsky (1943) that polycrystalline magnetostriction should depend not only on the magnetostrictive behaviour of single crystals but also on the elastic constants of the material, except in the limiting case in which the stress is uniform throughout the polycrystal. The situation has been reviewed recently by Lee (1955a) who concluded that the assumption of uniform stress is, in fact, the best approximation. Moreover, this conclusion has been convincingly supported by more recent experimental work by the author in which the polycrystalline magnetostriction constant of iron has been accurately determined and in which the

The corresponding spontaneous magnetostriction in the initial demagnetized state, $\bar{\lambda}_i$, may be obtained by repeating the integration of eqn. (43) subject to the condition that the domains are magnetized parallel to directions of easy magnetization, the β 's being again given by eqns. (63). When the directions are the quaternary axes, as in iron, the result is,

$$\bar{\lambda}_i = B_0 + \frac{1}{3}B_1 + \frac{1}{3}B_4, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66a)$$

whilst when the easy directions are the ternary axes, as in nickel,

$$\bar{\lambda}_i = B_0 + \frac{1}{3}B_1 + \frac{1}{3}B_3 + \frac{1}{9}B_4. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66b)$$

In neither case does the value of $\bar{\lambda}_i$ depend on assuming that the domains in each crystallite are initially divided *equally* between the various easy directions. Thus the fractional change in length of an ideal polycrystal between the demagnetized state and saturation is given by

$$\bar{\Lambda} = \bar{\lambda} - \bar{\lambda}_i = \xi + \eta \cos^2 x, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

where

$$\eta = \frac{2}{5}B_1 + \frac{3}{10}B_2 + \frac{12}{35}B_4 + \frac{3}{70}B_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad (68)$$

and where, for a material of positive anisotropy,

$$\xi = -\frac{2}{15}B_1 - \frac{1}{10}B_2 + \frac{1}{5}B_3 - \frac{26}{105}B_4 - \frac{1}{70}B_5 \quad . \quad . \quad . \quad . \quad . \quad (69a)$$

and, for a material of negative anisotropy,

$$\xi = -\frac{2}{15}B_1 - \frac{1}{10}B_2 - \frac{2}{15}B_3 - \frac{8}{315}B_4 - \frac{1}{70}B_5. \quad . \quad . \quad . \quad . \quad . \quad (69b)$$

It may be observed that if $B_3 = 0$ then $\xi = -\frac{1}{3}\eta$ and eqn. (67) may be put into the form

$$\bar{\Lambda} = \eta (\cos^2 x - \frac{1}{3}). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70)$$

Whilst it is reasonable to assume that $B_3 = 0$ for nickel and certain nickel-rich alloys (Bozorth and Hamming 1953), measurements on other single crystals (Bickford *et al.* 1955) have shown that B_3 —which is associated with an isotropic change in volume—may not be neglected for all cubic materials. Although eqn. (70) is generally accepted as governing the saturation magnetostriction of polycrystalline materials, the saturation magnetostriction constant, λ_s , being defined as $\frac{2}{3}\eta$, an examination of eqns. (68) and (69) shows that (70) will not be satisfied unless B_3 may be neglected. Moreover, the magnetoresistive behaviour of single crystals, which from symmetry considerations conforms to equations of the same form as those governing the magnetostriction, may not be represented by an equation of the same form as (70) since magnetoresistive measurements indicate that, even for nickel, the coefficient corresponding to B_3 may not be neglected.

3.3. The Polycrystalline Magnetostriction of Hexagonal Materials

For hexagonal materials the axes x_1 , x_2 , x_3 may again be assumed to be the $[1\bar{2}0]$, $[10\cdot0]$ and $[00\cdot1]$ crystallographic axes respectively. In order

If the spontaneous magnetostriction of the polycrystal is given by

$$\bar{\lambda} = \zeta + \eta [S(\alpha_1\beta_1)]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (76)$$

then $(\Delta\bar{\lambda})_2$ may be expressed in the form

$$(\Delta\bar{\lambda})_2 = -I_s^0 D_{ij}^0 \alpha_i \alpha_j \{(\zeta')_a + (\eta')_a [S(\alpha_1\beta_1)]^2\} - 2(\Delta\bar{\lambda})_1, \quad . \quad (77)$$

where $(\zeta')_a$ and $(\eta')_a$ are respectively the observed values, measured in high fields, of the apparent rate of change of ζ and η with respect to the applied magnetic field. The coefficients $(\zeta')_a$ and $(\eta')_a$ correspond to the $(P_i')_a$ of § 1.4. The evaluation of $(\Delta\bar{\lambda})_3$ (and also of $D_{ij}^0 \alpha_i \alpha_j$) is considerably simplified by the fact that the elastic energy of an isotropic solid has the form (8) when referred to *any* set of three orthogonal axes and hence these axes may be taken to correspond to the principal axes of the ellipsoidal specimen. The transformations (38) thus reduce to $x_i = x_i$ and, since the D'_{ijkl} are then given directly by equations such as (39), the quantity $(\Delta\bar{\lambda})_3$ may be obtained immediately from eqn. (40). Thus

$$(\Delta\bar{\lambda})_3 = (-\frac{1}{2} I_s^0 S_{klmn})_{ijmn} D'_{\alpha_i \alpha_j \beta_k \beta_l} \quad . \quad . \quad . \quad . \quad (78)$$

and again this expression is considerably simplified by the isotropic symmetry of the polycrystalline material.

As an example of the use of these formulae it is instructive to consider the special case of a polycrystalline spheroid magnetized to saturation in the direction x_3 of its axis of circular symmetry. For this case the demagnetizing coefficient D_{33} may be written in the form (Becker 1934)

$$D_{33} = D^0 \{1 - a[E_{33} - \frac{1}{2}(E_{11} + E_{22})]\}, \quad . \quad . \quad . \quad . \quad (79)$$

for D_{33} must remain unchanged by a uniform dilatation $E_{11} = E_{22} = E_{33}$. The quantity a may be evaluated from (39) and it has also been evaluated by Becker (1934) who gives a table of values of a and D^0 for spheroids of various eccentricities. The correction to the spontaneous magnetostriction due to the form effect is therefore given by

$$\begin{aligned} \Delta\bar{\lambda} = & \frac{1}{2} D^0 I_s^0 (S_{11} + 2S_{12}) - D^0 I_s^0 [(\zeta')_a + (\eta')_a \beta_3^2] \\ & - \frac{1}{4} a D^0 I_s^0 (S_{11} - S_{12})(1 - 3\beta_3^2). \quad . \quad . \quad . \quad . \quad (80) \end{aligned}$$

If the elastic compliance moduli are expressed in terms of the bulk modulus k and the rigidity modulus G then

$$\begin{aligned} \Delta\bar{\lambda} = & \frac{1}{2} D^0 I_s^0 \left[\frac{1}{3k} - \frac{a}{4G} (1 - 3\beta_3^2) \right] \\ & - D^0 I_s^0 [(\zeta')_a + (\eta')_a \beta_3^2]. \quad . \quad . \quad . \quad . \quad (81) \end{aligned}$$

Thus the longitudinal and transverse strains due to the form effect are respectively

$$(\Delta\bar{\lambda}) = \frac{1}{2} D^0 I_s^0 \left[\frac{1}{3k} + \frac{a}{2G} \right] - D^0 I_s^0 [(\zeta')_a + (\eta')_a] \quad . \quad . \quad (82a)$$

and

$$(\Delta\bar{\lambda})_t = \frac{1}{2} D^0 I_s^0 \left[\frac{1}{3k} - \frac{a}{4G} \right] - D^0 I_s^0 (\zeta')_a. \quad . \quad . \quad . \quad (82b)$$

The corresponding volume strain is

$$\Delta\bar{\omega} = \frac{1}{2}D^0I_s^{02}(1/k) - D^0I_s^0[3(\zeta')_a + (\eta')_a]. \quad . \quad . \quad . \quad (83)$$

3.5. Comparison with Experiment

Even in an ideal polycrystal with a random distribution of crystallites, the domains need not necessarily be distributed uniformly over all directions in the demagnetized state. A preferred domain orientation may arise either from shape anisotropy or from residual stresses in the polycrystalline specimen. It is therefore generally of little value to attempt a comparison of the theoretical and experimental values of the coefficient ξ of eqn. (67) until accurate measurements have been made on well-annealed and spherical polycrystalline specimens containing crystallites of no preferred shape. Such comparisons are, however, of some value for materials, such as cobalt, which have very high values of magnetic anisotropy. The coefficient η may, of course, always be unambiguously determined from measurements at saturation.

For nickel the generally accepted value (Lee 1955a) of η is -51×10^{-6} whilst the value obtained from eqn. (69b) by the substitution of the data of Bozorth and Hamming (1953) given in (55) is -51.3×10^{-6} with a probable error of 2.6×10^{-6} . Similarly for iron the figure obtained for η by inserting the values of (56) in eqns. (69a) and neglecting B_3 , B_4 and B_5 is -6.6×10^{-6} which is in reasonable agreement with the figure of -5.6×10^{-6} obtained by the author from measurements at saturation on polycrystalline iron.

At present there is no hexagonal material for which the constants of eqn. (23) have been measured. However, if it is assumed that λ is adequately represented by the second-order equation (51), then the corresponding values of the coefficients ξ and η of (67) may be evaluated from the experimental data of Bozorth and Sherwood (1954) given in (57). The figures obtained are $\xi = 25.7 \times 10^{-6}$ and $\eta = -97.0 \times 10^{-6}$, which appear to be in reasonable agreement with observations on polycrystalline cobalt, but as yet no accurate values have been obtained because such large fields must be applied to saturate polycrystalline specimens. The work of Nishiyama (1929), for example, who measured the longitudinal and transverse magnetostriction of polycrystalline cobalt in magnetic fields of up to 7,000 oe, shows that $\xi > 13 \times 10^{-6}$, $\eta < -53 \times 10^{-6}$ and that $\xi + \eta \simeq -60 \times 10^{-6}$. It may be observed in conclusion that, if the value for ξ deduced from the single crystal measurements is compared with $-\frac{1}{3}\eta = 32.3 \times 10^{-6}$, it may be seen that the saturation magnetostriction of polycrystalline cobalt is unlikely to conform even approximately to eqn. (70).

§ 4. THE FORCED MAGNETOSTRICTION

4.1. Introduction

Above the point of technical saturation, the total deformation of a single crystal (or polycrystal) arising from the combined existence of the

spontaneous magnetostriction and the form effect may be written in the form

$$\lambda + \Delta\lambda = [P_k - I_s^0 D_{ij}^0 \alpha_i \alpha_j (P_k')_a] S_k \\ + \frac{1}{2} I_s^0 S_{klmn} \left[D_{ij}^0 \frac{\partial \omega}{\partial E_{mn}} - \frac{\partial D_{ij}}{\partial E_{mn}} \right] \alpha_i \alpha_j \beta_k \beta_l. \quad (84)$$

The rate of change of this quantity with applied magnetic field may also be expressed in terms of the apparent forced magnetostriction constants introduced in § 1.4 so that

$$(P_k')_a S_k = \frac{\partial}{\partial H} (\lambda + \Delta\lambda) \\ = P_k' S_k + I_s^0 \frac{\partial I_s^0}{\partial H} S_{klmn} \left[D_{ij}^0 \frac{\partial \omega}{\partial E_{mn}} - \frac{\partial D_{ij}}{\partial E_{mn}} \right] \alpha_i \alpha_j \beta_k \beta_l, \quad (85)$$

where second-order terms have been neglected. It should be noted that I_s^0 is the value of I_s evaluated at the equilibrium lattice strain, so that although I_s^0 does not vary with strain it may nevertheless vary with the applied magnetic field. It may thus be seen that the apparent forced magnetostriction, as observed experimentally, differs from the true forced magnetostriction by a term which is non-zero only in so far as $\partial I_s^0 / \partial H$ is non-zero. When the orders of magnitude of the quantities appearing in this term are compared with the experimentally observed values of the $(P_k')_a$, it may be concluded that, in general, the difference between the true and apparent forced magnetostriction constants may be neglected.

In principle, the forced magnetostriction constants may be obtained directly by observing the dependence of strain on applied field, in high fields, or indirectly from the thermodynamic relations (33), that is from

$$P_k' S_k = \frac{\partial I_s}{\partial T_{kl}} \beta_k \beta_l + I_s^0 \frac{\partial \omega}{\partial T_{kl}} \beta_k \beta_l. \quad (86)$$

However, the experimental data at present available for single crystals only permit direct evaluation of the P_k' from forced magnetostriction measurements. Data exist for single crystals of iron (Calhoun and Carr 1955) and aluminium-iron (Hall 1957), the measurements being interpreted in both cases by assuming that the spontaneous magnetostriction may be adequately represented by eqn. (47). It is unfortunate that Hall perpetuated the assumption made by Calhoun and Carr that the forced magnetostriction is given by $\partial \lambda / \partial H$ rather than by $\partial \lambda / \partial H$, but both sets of data may nevertheless be readily interpreted in terms of the forced magnetostriction constants $C_i' = \partial C_i / \partial H$. Thus, for example, for iron (Calhoun and Carr 1955)

$$C_0' = 1.7 \times 10^{-10} \text{ oe}^{-1}, \quad C_1' = 0.94 \times 10^{-10} \text{ oe}^{-1}, \\ C_2' = -0.34 \times 10^{-10} \text{ oe}^{-1}, \quad 3C_0' + C_1' = 6.0 \times 10^{-10} \text{ oe}^{-1}, \quad (87)$$

the last constant being important since, to this approximation, it represents the forced *volume* magnetostriction of both single crystal and polycrystalline materials.

For polycrystals, the forced volume magnetostriction, $\bar{\omega}'$, has been measured directly for nickel (Azumi and Goldman 1954), iron (Snoek 1937, Kornetzki 1935), cobalt (Kornetzki 1934), and a range of nickel-iron alloys (Nagaoka and Honda 1902, Masiyama 1931, Kornetzki 1935). However, $\bar{\omega}'$ may also be estimated either from existing data on the variation of magnetic quantities with pressure or from observations of the thermal expansion anomalies associated with the destruction of the spontaneous magnetization. These two methods of estimating the forced magnetostriction are discussed in § 4.2 and § 4.3 respectively. From a critical examination of existing direct and indirect estimates of the forced volume magnetostriction of the common ferromagnetic metals, it would appear that the most probable values of $\bar{\omega}'$ are 6×10^{-10} for iron, 1.3×10^{-10} for nickel and 5×10^{-10} for cobalt.

4.2. *The Variation of Spontaneous Magnetization with Pressure*

For a polycrystal subject to a uniform pressure p the thermodynamic relation which corresponds to equations (33) may be written

$$\tau^0 \frac{\partial \bar{\omega}}{\partial H} = - \frac{\partial(\tau I_s)}{\partial p}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (88)$$

where $\bar{\omega} = 3\zeta + \eta$ is the fractional change in volume associated with the spontaneous magnetostriction. It may be noted that (88) may not be obtained immediately from the corresponding relations (33) involving the E_{kl} and T_{kl} since the equation

$$T_{11} = T_{22} = T_{33} = -p \quad . \quad . \quad . \quad . \quad . \quad . \quad (89)$$

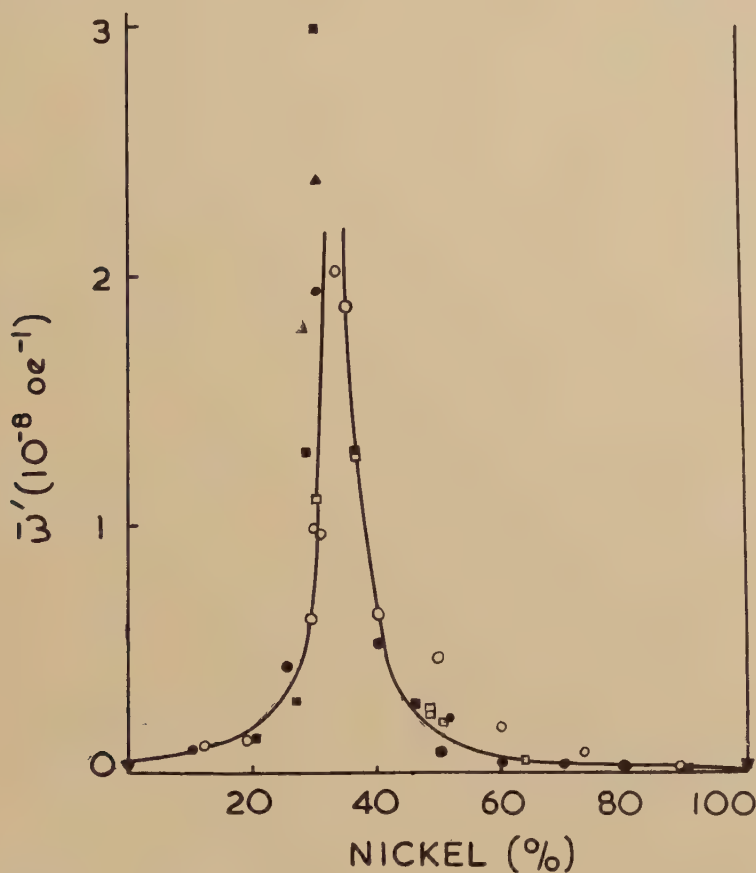
may be inconsistent with the assumption involved in partial differentiation with respect to one particular component of stress—namely, that the other components are considered to be constant. Equation (86) may thus be written in terms of the forced volume magnetostriction, $\bar{\omega}'$, as

$$\bar{\omega}' = \frac{\partial \bar{\omega}}{\partial H} = 3\zeta' + \eta' = \frac{I_s^0}{k} - \frac{\partial I_s}{\partial p}. \quad . \quad . \quad . \quad . \quad . \quad (90)$$

The measurement of either the forced volume magnetostriction or the variation of spontaneous magnetization with pressure presents considerable experimental difficulties because of the smallness of the effects being investigated. It is, in fact, only recently that accurate measurements of the effect of pressure on the spontaneous magnetization of a range of nickel-iron alloys by Guban (1958) have made possible a satisfactory assessment of the validity of eqn. (88). Guban's results, presented in terms of equivalent values of $\bar{\omega}'$, are shown in fig. 4 together with data derived from other measurements of both $\partial I_s / \partial p$ and $\bar{\omega}'$. The discrepancy occurring in the region of 30% nickel, between the forced magnetostriction and the pressure measurements, is undoubtedly due to the fact that alloys of approximately this composition are hard magnetically, fields of the order of 10 000 oersteds being needed to reach technical saturation. It should be noted, however,

that there is some evidence (Byelov 1950) to support the existence of a variation of $\bar{\omega}'$ with field in nickel-iron alloys containing approximately 30% nickel. The relatively high values of $\bar{\omega}'$ obtained, between 40% and 80% nickel, from pressure measurements by Ebert and Kussmann (1937) have

Fig. 4



Pressure results

□ Guban (1958).

○ Ebert and Kussmann (1937).

Volume Magnetostriction Results

■ Nagaoka and Honda (1902).

● Masiyama (1931).

▲ Kornetzki (1935).

▼ Snoek (1937).

Diagram showing values of $\bar{\omega}'$ obtained by various workers for nickel-iron alloys, either directly from measurements of the forced volume magnetostriction or indirectly from measurements of the pressure dependence of the spontaneous magnetostriction.

been attributed by Guggen to experimental errors associated partly with the presence of the order-disorder transition which occurs in this range of compositions.

The pressure dependence of the Curie temperature, Θ_c , may be more readily measured than that of the spontaneous magnetization but its connection with $\bar{\omega}'$ is known with considerably less precision. From thermodynamic reasoning, using a molecular field treatment, Kornetzki (1935) derived a formula for the variation of Curie temperature with pressure which may usually (Lee 1955 a) be written in the form

$$\frac{\partial \Theta_c}{\partial p} = \Theta_c \bar{\omega}' / \Theta \frac{\partial(\tau I_s^0)}{\partial \Theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

where Θ is the absolute temperature. Although this formula is in agreement with certain experimental data, such as a large decrease of Θ_c for 30% nickel-iron alloys which corresponds to the observed increase in $\bar{\omega}'$, it seems improbable that it is correct in detail. The effect of refining Kornetzki's theoretical treatment has been reviewed recently by Lee (1955 a) who concluded that the agreement between theory and experiment is poor, in some cases disagreeing even as to sign.

4.3. *The Thermal Expansion Anomaly*

Quantitatively, the thermal expansion anomaly of a polycrystal may be characterized by a quantity δ which is defined as the fractional change in length which accompanies the appearance of the spontaneous magnetization. For a polycrystal in the ideal demagnetized state δ is given by the formulae for $\bar{\lambda}_i$ derived in § 3.2 and § 3.3. However, measurements of δ show that, in general, it is considerably larger than the anisotropic-isotropic and anisotropic-anisotropic magnetostriction constants so that the thermal expansion anomaly is principally associated with the isotropic-isotropic and isotropic-anisotropic constants. For example, for nickel, $\delta \simeq -2 \times 10^{-4}$ whilst $\bar{\lambda}_i \simeq B_0 + \frac{1}{3}B_1$ and $\frac{1}{3}B_1 \simeq -2 \times 10^{-5}$. As a rough approximation it is therefore permissible to assume that $\delta = B_0$ for cubic materials. For cobalt and gadolinium $\delta = R_0 + \frac{1}{3}R_1$ but the relative importance of the two constants R_0 and R_1 is at present unknown and can, of course, only be determined from measurements on single crystals.

The most direct method of estimating δ is to measure the temperature variation of the true coefficient of thermal expansion, $(\partial l / \partial \Theta) / l$, of a polycrystalline specimen of length l . The deformation of the specimen associated with the appearance of the spontaneous magnetization may then be seen superimposed on the normal thermal expansion as shown in fig. 5. For nickel the quantity δ is negative and is equal to the area between the two curves shown in fig. 5. This area is, however, very dependent on the position of the broken curve which serves as a base line and represents the normal (i.e. non-magnetic) thermal expansion coefficient. The first estimate of δ was made, for nickel, by Williams (1934) who used as a base line his own data at temperatures from room temperature to about 300°C

and those of Hidnert (1930) for temperatures considerably above the Curie point. The broken curve of fig. 5 is, in fact, obtained by a different process which may be explained as follows.

Since the normal thermal expansion of a solid is due to anharmonicity of the interatomic forces it may be calculated, in principle, from the observed elastic anharmonicity (Sheard 1958). In practice, however,

Fig. 5

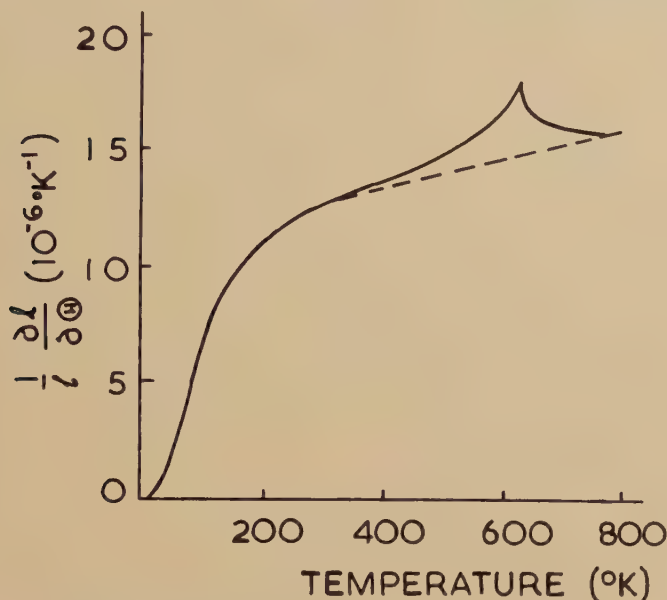


Diagram showing the variation with temperature of the true coefficient of thermal expansion of nickel. The broken curve is a Grüneisen plot which fits the experimental results (full line) of Nix and MacNair (1941) at low temperatures.

calculations of thermal expansion have relied upon a single phenomenological parameter as an average measure of the anharmonicity, namely the Grüneisen constant g (Grüneisen 1926). From statistical mechanics (Slater 1939), a factor g_i may be derived for each vibrational frequency ν_i where

$$g_i = -\frac{\tau^0}{\nu_i} \frac{\partial \nu_i}{\partial \tau} = -\frac{\partial \ln \nu_i}{\partial \ln \tau}. \quad (92)$$

If it is assumed that the frequency spectrum is determined entirely by the limiting frequency ν_{\max} characterized by the Debye temperature, then the g_i are all the same and are equal to

$$g = -\frac{\partial \ln \nu_{\max}}{\partial \ln \tau}. \quad (93)$$

By using thermodynamic relationships, it may then be shown that the coefficient of thermal expansion is

$$\frac{1}{l} \left(\frac{\partial l}{\partial \Theta} \right) = \frac{g\chi C_{\tau^0}}{3\tau^0}, \quad (94)$$

where χ is the isothermal compressibility and C_{τ^0} the heat capacity at constant volume τ^0 . The broken line of fig. 5 was obtained by Nix and MacNair (1941) by fitting eqn. (94) to their data for nickel at temperatures around and below room temperature. The value thus obtained for δ was -3.65×10^{-4} which may be compared with the value obtained by Williams of -0.92×10^{-4} for nickel of comparable purity. However, it has been known for some time that the assumption that the g_i can be represented by an average value g is incorrect, for the work of Bijl and Pullan (1955) has shown that g may vary with temperature in contradiction to eqn. (94). Thus, when it is remembered that the true thermal expansion coefficient depends on the rate of change with temperature of the experimentally measured expansion of the specimen and is therefore very sensitive to experimental error, then it may be concluded that estimates of δ obtained by the process outlined above should be treated with some caution. The data available for materials other than nickel are rather unreliable but approximate values of δ for iron and cobalt are respectively $+2 \times 10^{-4}$ and -1×10^{-2} .

The importance of the measurement of δ in estimating $\bar{\omega}'$ is associated with the equation

$$\delta = (aI_s^{02} + bI_s^{04}) \frac{\partial J}{\partial \tau}, \quad (95)$$

(where a and b are constants and J is a measure of the exchange interaction) derived from theoretical considerations by Fowler and Kapitza (1929). The quantity $\partial J / \partial \tau$ is unknown but according to Néel (1939) eqn. (95) may be represented to a good approximation by

$$\delta = cI_s^{02}, \quad (96)$$

so that by substituting for the constant c in terms of $\partial \delta / \partial H$

$$\frac{\partial \delta}{\partial H} = 2 \frac{\delta}{I_s^0} \frac{\partial I_s^0}{\partial H}. \quad (97)$$

It is commonly supposed (Lee 1955 a) that $\partial \delta / \partial H$ may be replaced, in this equation, by $\frac{1}{3} \bar{\omega}'$ so that measurements of δ and $\partial I_s^0 / \partial H$ permit an indirect evaluation of $\bar{\omega}'$. However, although for cubic crystals δ is approximately equal to B_0 , the rate of change of δ with respect to H is not given by $B_0' = \partial B_0 / \partial H$ since B_0' is not observed experimentally to be much larger than the other B_i' . Thus eqn. (97) is less useful than is commonly supposed for it permits measurements of δ and $\partial I_s^0 / \partial H$ to be correlated with the observed forced magnetostriction of single crystals rather than with measurements of $\bar{\omega}'$ for polycrystals. The experimental data at present available do not permit an accurate verification of eqn. (97) but it may be

used to predict the correct order of magnitude of the polycrystalline forced magnetostriction of nickel (Lee 1955 a).

Although the figures given above for δ may not be readily used to evaluate $\bar{\omega}'$ they may be employed, in conjunction with the experimental values of the magnetostriction constants collected in § 2.6 and of the elastic coefficients given in the table, to evaluate the magneto-elastic coupling constants of § 2.2 and § 2.3. For the common ferromagnetic metals, the results of this procedure are as follows.

If the spontaneous magnetostriction of nickel is represented by the fourth-order equation (43), the magneto-elastic coupling constants of eqn. (17) are given by

$$\begin{aligned} L_0 &\simeq 11 \times 10^8 \text{ dyne cm}^{-2}, & L_1 &= 100 \times 10^6 \text{ dyne cm}^{-2}, \\ L_2 &= -25 \times 10^6 \text{ dyne cm}^{-2}, & L_3 &= 32 \times 10^6 \text{ dyne cm}^{-2}, \\ M_0 &= 90 \times 10^6 \text{ dyne cm}^{-2}, & M_1 &= -19 \times 10^6 \text{ dyne cm}^{-2}, \end{aligned} \quad (98)$$

the constant L_0 being evaluated from the equation

$$L_0 = (\frac{1}{3}B_3 - \delta)(C_{11} + 2C_{12}) + \frac{1}{3}B_1(C_{11} - C_{12}) + \frac{1}{9}B_4(C_{11} - 7C_{12}). \quad (99)$$

Similarly, if the spontaneous magnetostriction of iron is represented by the second-order equation (47),

$$\begin{aligned} L_0 &\simeq -10 \times 10^8 \text{ dyne cm}^{-2}, & L_1 &= -30 \times 10^6 \text{ dyne cm}^{-2}, \\ M_0 &= 73 \times 10^6 \text{ dyne cm}^{-2}, & & \end{aligned} \quad (100)$$

the constant L_0 being evaluated from the equation

$$L_0 = -\delta(C_{11} + 2C_{12}) + \frac{1}{3}C_1(C_{11} - C_{12}). \quad (101)$$

If the spontaneous magnetostriction of cobalt is represented by the second-order equation (51), the magneto-elastic coupling constants of eqn. (22) are given by†

$$\begin{aligned} 11.5L_0 + 6.0M_0 &\approx 10^{12} \text{ dyne cm}^{-2}, \\ L_1 &= 16 \times 10^7 \text{ dyne cm}^{-2}, & L_2 &= 24 \times 10^7 \text{ dyne cm}^{-2}, \\ M_1 &= -26 \times 10^7 \text{ dyne cm}^{-2}, & M_2 &= 35 \times 10^7 \text{ dyne cm}^{-2}. \end{aligned} \quad (102)$$

It has been assumed in calculating values of L_0 and M_0 in eqns. (98), (100) and (102) that measurements of δ have been obtained with a polycrystal in the *ideal* demagnetized state so that δ may be obtained from eqns. (66) and (72)—an assumption which is justified by the degree of uncertainty involved in the experimental estimates of δ .

† The approximate nature of the relation involving L_0 and M_0 is principally due to the existence of a phase change between room temperature and the Curie point.

ACKNOWLEDGMENTS

The author wishes to thank Professor L. F. Bates for his interest and encouragement and Dr. E. W. Lee for many valuable and interesting discussions, and to express his gratitude to Mr. B. Adkins for his helpful comments on the manuscript.

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Soft Magnetic Materials

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§ 1. INTRODUCTION

THE distinction between 'hard' and 'soft' magnetic materials is to a large extent arbitrary since it is based primarily on their ultimate technical applications. There are two well-defined groups of materials which find practical use: 'soft' material in which the coercivity is less (usually much less) than 2 oersteds and 'hard' materials in which it is over 50 oersteds. The latter almost invariably find application as permanent magnets. The uses of the former are more diverse and for this reason soft magnetic materials cover a wider range of physical properties and magnetic behaviour than do their hard counterparts. Furthermore they are often employed under conditions of alternating magnetization for which their particular electrical properties may be just as important as their magnetic ones. Consequently, although the possession of a high permeability and low coercive force is a necessary requirement of a good soft magnetic material, it is unlikely to be a sufficient condition or even an over-riding one. Highly purified iron for example has magnetic properties not greatly inferior to those of the best soft magnetic alloys. Two factors militate against its use as a soft magnetic material either at present or in the foreseeable future. In the first place the elaborate process of purification is too costly to be carried out commercially and secondly its electrical resistivity is too low to make it a useful transformer material. Thus it is not possible to divorce entirely the pure physical properties of soft magnetic materials from their ultimate application or from the technical requirements which led to their development. Since it is anticipated that this review will be read chiefly by physicists the physical viewpoint will be stressed at the expense of the technical one. To be oblivious of technical requirements and the final application of these materials is however to run the risk of that over-simplification which eventually leads to misunderstanding.

Considerable advances on soft magnetic materials have been made since the end of the war and it is fortunate that the subject has already been

reviewed in some detail. Bozorth's book *Ferromagnetism* published in 1951 contains a comprehensive account of the materials and their properties and thus adequately presents the situation existing roughly in 1950. The present review will therefore take his book as a starting point and concentrate mainly on developments which have taken place since it appeared. The most important of these developments is the widespread study and use of ferrites and it is necessary to consider the magnetically soft ferrites in some detail. Two useful articles on ferrites have, however, appeared elsewhere (Fairweather *et al.* 1952, Smit and Wijn 1954) and so this review will consider only those aspects of ferrites which have developed since 1953. Further, the use of ferrites in microwave apparatus is covered by a recent and comprehensive paper (Fox *et al.* 1955) and a full bibliography (Clarricots *et al.* 1957) so that this highly specialized subject may be omitted from the present review.

Magnetic properties may be conveniently divided into two classes: *Intrinsic* properties (such as spontaneous magnetization, crystal anisotropy and magnetostriction constants) are independent of the exact condition of the specimen and the method of its preparation, and are affected only by temperature, hydrostatic pressure (this effect usually is very slight) and, in alloys in which ordering takes place, by the degree of atomic ordering†. Secondary magnetic properties, such as the coercivity and initial permeability, are strongly dependent on the presence of impurities and mechanical stresses and on their distribution throughout the material. This usually unknown dependence on a large number of variables often makes the interpretation of experiment ambiguous, for it may not be clear whether an observed effect is characteristic of a material or merely of the methods which have had to be used in its preparation. This point is discussed at greater length in § 2.

A further complication arises from the fact that all the soft magnetic materials actually in use are alloys. This observation, however trivial it may seem, is of the utmost importance. Stoichiometric or near-stoichiometric alloys‡ may undergo order-disorder transitions. As a result both the crystal anisotropy and magnetostriction constants may vary and thus affect the secondary magnetic characteristics. Moreover, spatial fluctuations in composition or the degree of order may be expected to introduce magnetic inhomogeneities into the material. This, however, is not all, for there is a further possibility of magnetic ordering even in alloys whose compositions are far from stoichiometric. This is discussed more fully in § 7.4; at present we merely observe that it adds one more variable to the factors affecting low-field properties.

† The crystal anisotropy may be profoundly influenced by magnetic ordering (§ 7.4) if this takes place.

‡ Certain alloys, notably the binary nickel-irons, seem to undergo ordering over a very wide range of composition (Wakelin and Yates, 1953). The intrinsic magnetic properties are usually significantly affected by ordering only when the composition is nearly stoichiometric. Secondary magnetic properties are usually much more sensitive to ordering and exhibit an effect over a much wider range of composition.

For this reason a criticism which can be levelled at a great deal of published work is the unsatisfactory choice or identification of the magnetic materials used in experiments. Of the metallic soft magnetic materials, the most interesting are precisely those in which the exact composition, preparation, and heat treatment are the most critical; similarly, the number of possible variables in the preparation of a ferrite is large, and they may lead to differences not only in composition but in such properties as the porosity, which in turn affect the magnetic properties. It is, however, exceptional to find the methods of preparation fully described in a published account.

It does not seem to be generally realized that the trade names of materials are unreliable as an identification. The same name may be used, at different times or in different countries, for materials which, though they have broadly similar properties in everyday use, may appear appreciably different in the conditions of a closely controlled experiment. Such trade names are often retained unchanged when improved alloys are introduced, and in thirty years may have referred to half a dozen different alloys. The extent of batch-to-batch variation in some alloys is also such that materials having widely differing properties appear under the same name.

§ 2. PREPARATION AND FABRICATION

In conformity with the outlook adopted in the Introduction we give here a brief survey of the techniques employed in making soft magnetic alloys.

2.1. *Preparation of Alloys*

Metallic materials are normally made by melting and casting. During melting they must be protected from oxidation, and for this purpose a flux is used to cover the surface of the melt, and deoxidants such as magnesium are added. So made, alloys may depart from the intended composition in two ways: by the inclusion of impurities derived either from the flux or from the crucible, and by containing the major constituents in incorrect ratios as the result of either preferential evaporation or segregation during solidification.

Melting either in a vacuum or in a protective atmosphere (such as helium) overcomes difficulties due to fluxes. This process has been used for the commercial production of a number of alloys, including Superalloy and Permenorm 5000 Z; and it is also suitable for work on a laboratory scale. Melting in an argon arc has also been successfully tried in the laboratory.

A process which, if applicable, overcomes all the difficulties mentioned is that of powder metallurgy, in which powders of the separate constituents are thoroughly mixed, then pressed into a block and sintered at a temperature of the order of 1300°C; at this temperature the various metals alloy by diffusion but without melting (Richards *et al.* 1957, Walker *et al.* 1954, Thien-Chi 1954). The metals which can be alloyed in this way include iron, nickel, cobalt, copper and molybdenum, but not aluminium. Manganese can be added to some alloys but not to others. The precision of composition obtainable in this way is believed to be about 0.05% (Lynch

1954) and the main impurities are likely to be carbon and unwanted metals present in the raw materials. Since the precision of chemical analysis is only about 0.1%, powder metallurgy offers a more precise control of composition than the conventional method, which is to use chemical analysis to determine the composition actually obtained as the result of melting.

The powder-metallurgy process has been used both in laboratories and for commercial production (Kerr 1957).

2.2. Annealing

The magnetic softness of most alloys depends on their being annealed. Strictly, this term implies merely that they should be allowed to recrystallize after the mechanical working which is usually necessary in shaping a specimen; a few minutes at a temperature of the order of 900°C would suffice for this. Oxidation must be prevented, so a protective atmosphere is used—usually of hydrogen for laboratory experiments, but in commercial production usually of cracked ammonia (which can easily be kept very free from oxygen and steam) or of town's gas.

It has been known for a long time, however, that the coercivity of many materials (including pure iron) can be reduced by further periods of annealing, even after recrystallization is complete. Obviously some other process is also taking place—presumably the removal of certain impurities such as carbon and nitrogen.

Two precautions may be necessary in carrying out an anneal of long duration. First, if the material contains elements such as chromium or silicon whose oxides are not easily reducible in hydrogen, then oxygen and water must be carefully excluded from the protective atmosphere. Second, silicon, unless intended to be a constituent of the material, must be prevented from entering it from the crucible or from the annealing furnace. The maximum permissible water content of the annealing atmosphere may correspond to a dew-point of the order of -50°C (Richards *et al.* 1957).

2.3. Grain-orientation

In some polycrystalline materials, properties similar to those of single crystals can be obtained by systematic orientation of the axes of the individual crystals. The standard procedure for achieving this is to set up a deformation texture in the material by severe cold-working followed by recrystallization. An important variant of this treatment is 'secondary recrystallization'—that is, the growth, at the expense of crystals having some other orientation, of a group of similarly oriented crystals which initially form only a small proportion of the whole. Since most soft magnetic materials find ultimate use as transformer cores they are usually fabricated in thin sheet form and the cold work is conveniently carried out by rolling. Rolling textures are set up only if the degree of reduction is sufficiently great. For 50/50 nickel-iron this may be 96%, after which the material

develops a deformation texture in which the minute crystals are aligned with [110] axes along the rolling direction. The material is then given any further mechanical working which may be needed to produce the required shape of specimen (e.g. punching or coiling), and is finally annealed at a temperature (e.g. 1050°C) which allows primary but not secondary recrystallization. For material which has been melted and cast, the annealing temperature is critical and has to be determined by experiment for every individual batch (Both 1948; Crede and Martin 1949); in material made by powder metallurgy, however, secondary crystallization does not occur so readily, presumably because of the absence of some particular impurity, which would facilitate secondary recrystallization and a wider range of annealing temperatures is permissible. After this treatment the texture is (100) [001], so that the crystal axes lie with four [100] directions in the plane of the strip; if secondary crystallization occurs, this may no longer be so.

Savitski (1958) claims to have improved the range of permissible annealing temperatures by the addition of up to 1% manganese, accompanied by about 0.15% oxygen and possibly 0.25% silicon; but Both (1948) has said that there is "no metal which upon addition to 50% nickel-iron would yield improved quality", and that silicon is harmful.

A systematic deformation texture in 4-79 Permalloy, when rolled to thicknesses of a few microns, is stated (Koh 1958) to be (110) [335] and to have easy directions of magnetization making angles of 14° with the rolling direction. After annealing a complex recrystallization texture develops in which there are no easy directions in the plane of the sheet.

In some other alloys these methods of rolling and heat-treatment, while producing orientation, do not markedly change the magnetic properties (Randall and Scholefield 1953).

A rather more complicated case of grain-orientation is provided by body-centred cubic alloys of which the best-known magnetic example is 3% silicon-iron. This is used extensively for transformer sheet; when produced by hot-rolling, it contains randomly orientated crystal grains and is magnetically isotropic. Goss (1935) showed that cold-rolling orients the grains systematically. On annealing, they may produce either a (110) [001] or a (100) [001] texture by secondary recrystallization, according to the degree of rolling and the annealing temperature (Assmus *et al.* 1957). The general nature of the alignment process is outlined by Bozorth (1951) but the exact method by which nuclei are provided for secondary recrystallization, without at the same time losing the desirable magnetic properties already possessed by the un-oriented alloy, has not been published.

2.4. Magnetic Annealing

Another way of obtaining quasi-single crystal characteristics from what is essentially polycrystalline material is to cool the material from a high temperature in the presence of a magnetic field. This process, usually known somewhat inaccurately as magnetic annealing, promotes easy

directions along the direction of the field and has the effect of increasing the maximum permeability (but not the initial permeability) and making the hysteresis loop nearly rectangular. Magnetic annealing may be used either in conjunction with grain-orientation as in 50/50 nickel-iron, or without, as in Perminvar and 65/35 nickel-iron. It has been used successfully with 6.5% silicon-iron (Goertz 1951) and there seems no reason in principle why it should not be used with the new cube-texture silicon-iron. Materials treated in this way are of course uniaxially anisotropic but for certain applications this may not be a disadvantage. The mechanism of magnetic annealing is now believed to be fairly well understood and is discussed at greater length in § 7.4.

The techniques employed for magnetic annealing are quite straightforward. The range of temperatures in which the treatment is applied is given by Bozorth as approximately 600 to 300°C, but may in fact be rather narrower. Prolonged treatment at a constant temperature can produce a similar result. The magnetic field need not greatly exceed the coercive force of the material; it is usual to provide about 10 Oe. The winding may be by a single turn carrying a heavy current, which may be either direct or alternating. Multi-turn windings are inconvenient to apply, and are liable to damage because copper (unless of a special oxygen-free grade) is embrittled by the hydrogen atmosphere which is needed to protect the core at these temperatures.

2.5. *Evaporated-on Films*

Thin films of magnetic material have been prepared by deposition from vapour. The process can be used for iron or nickel, or for an alloy of approximately 80/20 nickel-iron which, by good fortune, is a particularly interesting one. The thicknesses which have been reported range from 30 to 10 000 Å. These films are usually deposited on a base-plate heated to about 300°C, and in a magnetic field (Blois 1955); if so made, they have almost perfectly rectangular hysteresis loops and are of interest for applications as storage and logical devices in computers. The rectangular loop can be observed even when the magnetic circuit is not closed, because the demagnetizing factor is low for so thin a specimen. The loop is of course rectangular only when the testing field is in the same direction as that during deposition; but Williams and Sherwood (1957), and Mitchell (1958), report that a new preferred direction can be induced by annealing in a magnetic field along a new axis (this of course is possible only if the base material will withstand the annealing temperature).

§ 3. METHODS OF INVESTIGATION

It is not proposed in this section to enter into a lengthy survey of general measuring techniques. A very large number of these are common currency among magnetic determinations and are in no way specific to the type of magnetic material under investigation. This is particularly true of

intrinsic magnetic properties; but secondary magnetic properties, because of the larger range they exhibit, may demand techniques of a more specialized nature. The softest magnetic materials present their own investigational problems and these stem from two main causes. In the first place they possess their interesting magnetic properties because of a unique combination of low magnetic anisotropy and low magnetostriction. On this account investigation is difficult, since for the operation of the methods which would normally be employed, at least one of these quantities must be large. Foremost among these methods is the direct observation of domain boundaries using magnetic colloid or similar techniques; others, of more limited application but sometimes of great value nevertheless, include studies of magnetostriction and thermomagnetic effects. The second difficulty is of a different kind and arises from the fact that anyone undertaking to investigate soft magnetic materials must in practice often be content to work with small samples having small cross-sectional area. The extreme example of this is afforded by the investigation of evaporated metal films. With other materials the situation is rarely so acute but often sufficient to raise severe problems of sensitivity and signal-to-noise ratio.

From the purely technical standpoint the characteristics most frequently recorded can be found by a measurement of the hysteresis loop, the initial permeability† and the losses under alternating field conditions. A surprisingly large amount of information may be obtained from a perusal of hysteresis loops and it is appropriate therefore to deal first with methods of measuring them.

3.1. *B/H Loops*

With high-permeability alloys the outstanding requirement is the use of a sample having a closed magnetic circuit; otherwise demagnetization effects will ensure that the measured characteristics are determined almost entirely by the shape of the sample and it is extremely unlikely that a demagnetization correction can be made of sufficient accuracy to restore any meaning to the observations. This requirement naturally becomes less stringent when the material investigated is thin, and for evaporated films of a few thousand Ångströms thickness may cease to exist altogether.

3.1.1. *Ballistic galvanometer methods*

The usual quasi-static methods using a ballistic galvanometer are usually satisfactory provided the volume of material under investigation is

† The use of permeability rather than the susceptibility throughout this article is only partly in deference to standard engineering practice. Electromagnetic phenomena are determined by the permeability of a given substance rather than its susceptibility and although the decomposition of μ into $4\pi k + 1$ may be desirable from certain physical standpoints, the urge to do this becomes weakened by the realization that in some modern alloys the initial permeability may exceed 10^5 .

sufficiently great. Sensitivity may be improved by the use of a photo-electric galvanometer amplifier (Hill 1948, Troughton 1958). There is some doubt about the speed with which B/H loop measurements should be made (Parkin 1955). A sudden change of field produces a change of flux which is not instantaneous; in some materials only about 95% of the change may occur in the first second. In such a case, a loop measured with a galvanometer of short period does not represent a fundamental property of the material and inconsistent results may be obtained if the loop is measured step-by-step in steps first of one size and then of another. Equally, a loop measured with apparatus of long time-constant may not represent properties which are of practical interest.

An anomaly is sometimes† observed in which the normal induction curve, or the tips of a minor loop, lie outside the loop observed with a large field. (This is unexpected because it implies that the specimen, when in a state corresponding to the intersection of the loops, can 'remember' which one it is following.) Snoek (1947) showed that this would occur in bar-shaped or ellipsoidal specimens if the magnetizing current were varied too rapidly. If the current is brought to its full value before eddy currents within the specimen have died away, which may take a time of the order of 1 sec, then the specimen behaves temporarily as a tube rather than as a bar, and has a lower demagnetizing coefficient than that for its true shape. Consequently the flux reaches a high value from which it falls as the conditions become stable, and the material near the surface of the specimen is on the descending limb of a minor loop rather than on the ascending one. This gives rise to an apparently low coercivity and high remanence. Snoek therefore recommends the use of a non-magnetic conducting tube around the specimen but inside the magnetizing winding (an arrangement which Pierce had used in 1912 without realizing why it changed his results).

This effect would not be expected in ring specimens; but Kayser (1949) found it in hot-rolled silicon-iron rings, and thought it might be due to slight anisotropy of the specimen or non-uniformity of the winding. Both Snoek and Kayser made sure that the effect was not being produced by oscillations in the magnetizing circuit, which might provide a temporarily increased field. Nevertheless, an effect of this kind may be a genuine property of the material, as will appear below (§ 7).

3.1.2. *Mechanical tracing of B/H loops*

The step-by-step method of measuring B/H loops, though simple, is tedious and several successful attempts (Cioffi 1950, Tebble 1953, and Brockman and Steneck 1954) have been made to construct apparatus in which the desired result is achieved automatically, either slowly or at frequencies up to about 1 kc/s.

The mechanical tracing of a loop on paper usually needs a period of the order of 30 sec. The main problem in the design of the apparatus is to

† "More often than not."—Spooner (1927).

devise an integrating circuit which will remain accurate over so long a period of time and which can accept signals of widely varying amplitudes at various parts of the loop. The usual solution is to use a galvanometer and photo-cell and to govern its response by a negative feedback circuit including a differentiating network.

Unfortunately, one of the main uses of these loop-plotting or display devices would be in the study of rectangular-loop materials. But if the field is varied either uniformly or sinusoidally, the range of the signals to be handled by the integrator and amplifiers, which are proportional to dB/dt , is enormous, and it is difficult to avoid the distortion of low-level signals by noise or of high-level signals by the overloading of valves. Further, the linear speed at which the loop is traced varies from point to point, and if sufficient time is allowed for a mechanical recorder to trace the nearly vertical parts of the loop the time required for the whole loop may become impracticably long. The solution to this problem probably lies in the automatic control of the applied field from the dB/dt signal; once more, however, a loop plotted in these conditions may not relate to any practical condition of use.

An alternative method of tracing the a.c. loop is to use a secondary winding whose output is mechanically switched by contacts operated at the supply frequency and at any chosen point in the cycle (Geyger 1938, 1955). The moment of switching is slowly varied through the whole cycle of magnetization. This is the basis of the 'Ferrometer'. The peculiarity of this method is that although the loop is traced slowly it is nevertheless that relating to alternating conditions.

3.1.3. Oscillographic display

Oscillographic display of B/H loops may be desirable for two reasons; it is more sensitive than the step-by-step galvanometer method and it frequently refers more closely to practical conditions.

Suitable apparatus has been constructed in a number of laboratories. The displays usually correspond to frequencies of 50 c/s or more, and do not necessarily agree with the 'd.c.' loops for the materials. The difficulties to be overcome in such apparatus are the construction of amplifiers in which there is negligible phase-shift at the relevant frequencies, and (especially if the specimens to be measured are of small cross section) in which noise and unwanted couplings with other circuits do not interfere with signals at low levels. Dunstan and Somerville (1958) discuss the design of integrating circuits suitable for this purpose. Crittenden *et al.* (1951) describe apparatus for use with specimens consisting of thin films.

An alternative to a B/H loop is a loop showing dB/dH against H (Hobson *et al.* 1947), which of course contains the same information though in a different form. It is somewhat easier to produce electronically, and if the apparatus is unable to deal with any particular sample having extreme properties the fault will be more obvious than in the B/H loop obtained by integration.

3.2. *Direct Observations of Magnetic Domains*

There are two separate and distinct ways of observing ferromagnetic domains. The method most widely used is to observe the surface field at the domain wall. This is the principle behind the magnetic colloid technique (for a review see Bates 1954) and the electron scattering methods. The Permalloy-probe method of Kaczer (1955) also makes use of this principle. The second type of method makes use of the magnetic Kerr Effect. This method measures the direction of magnetization within a domain. It was clearly demonstrated long ago by Kundt (1884) that the effect is one associated with the reflecting surface itself and not with surface fields. All these methods have in common the fact that only the domains which intersect the surface can be investigated. There exists no direct method of observing the domains beneath the surface, except possibly in the transparent yttrium-iron garnet.

3.2.1. *Magnetic colloid techniques*

If a domain wall intersects the surface of a ferromagnetic substance, the normal component of I_s should remain continuous across the wall. It follows that a component of I_s will exist at right angles to the surface where the wall intersects it. This normal component of I_s produces a surface field which from the viewpoint of the wall is essentially a demagnetizing field tending to rotate the spins within the wall so that the surface field is decreased. This process will go on until the decrease in magnetostatic energy is offset by the increase in the domain wall energy. This increase will come partly from the anisotropy energy and partly from the exchange energy. A rigorous general treatment of domain wall energies taking surface effects into account would appear to be difficult. Néel (1955) and Kaczer (1957) have considered the effects of magnetostatic terms on the energy and thickness of domain walls in very thin specimens such as evaporated films, and it seems that such effects are likely to be of similar importance in materials with very low anisotropy and consequently with very broad domain walls. It is, in any case, intuitively obvious that for substances with low anisotropy there will be a tendency for the domain walls to be distorted at the surface and the surface field thereby reduced. In consequence the magnetic force on a colloidal particle on the surface of a material having low anisotropy is small and the domain walls, even if they exist, are not sharply delineated by the colloidal particles as they are in, say, cobalt or 3.5% silicon-iron. Experimentally it appears that, with conventional colloid techniques, the likelihood of observing well-defined domain walls becomes rather small when the anisotropy is less than about 10^4 ergs/cm³. These facts are mostly well known and it comes as a surprise to find that domain patterns have been readily observed on a number of relatively low anisotropy ferrites (Bates, Craik and Griffiths 1958). The authors' success may be due partly to the development of new types of colloid usually possessing much smaller particle size than is obtained using

the standard recipes of Bozorth (1951) and Elmore (1938). It is not easy to see why the ferrites should be specially favoured and it may be that the low-anisotropy metallic ferromagnetics would repay further investigation with the improved techniques.

3.2.2. *Electron beam techniques*

The surface fields existing near domain boundaries may be quite large and may be used to scatter a collimated beam of electrons. Observation of the scattered beam can in principle be used to study local variation in the surface fields, in other words the domain structure. This technique, first employed by Germer (1942), has recently been developed by Blackman and his associates (Blackman and Grünbaum 1956, 1957). Apart from the possibility of severe difficulties of interpretation, when the domain structure to be investigated is fine the method appears to have one definite advantage in that the scattering of an electron beam is proportional to $\int H dl$, which means that the weak surface fields can be readily detected provided that they exist over a sufficiently large volume. In this way Blackman *et al.* (1957, 1959) were able to observe scattering from surface fields due to the parasitic magnetization believed to be associated with domain walls in α -Fe₂O₃.

Another possible technique is electron mirror-microscopy (Mayer 1958). A beam of electrons is reflected by the local magnetic field close to the surface of the specimen, reinforced by an electric field applied between the specimen and the source of electrons. The pattern produced in the reflected beam is not strictly an image of the magnetized surface; Mayer describes it as an "electron-optical schlieren-picture". The specimen must have a flat surface, or the picture will be that of its shape rather than of its magnetization.

3.2.3. *Magnetic probe methods*

Any system which responds to a magnetic field can in principle be used to map the surface fields on a ferromagnetic specimen. Apart from the advantage that they can be used over a wide temperature range, probe techniques are severely limited in application by the fact that the size of the probe is often large compared with the domain size under investigation. In the Permalloy probe method of Kaczer (1955) a thin narrow strip of Permalloy is held vertically and is carefully machined to a point at the end nearest the surface under investigation. When set into transverse vibration the probe becomes magnetized by the surface fields and this is detected by a coil placed round the probe. The sensitivity is such that domain walls on 3% silicon-iron can be detected but any detailed mapping of the walls is prevented by stray fields due to surface imperfections. A method which might prove more sensitive would be to use a second-harmonic device such as is employed in the fluxgate, but no improvement in distinguishing domain walls from surface imperfections is to be expected. Some of these probe

methods might be more successful with substances possessing a good surface, such as evaporated films, but we do not know of any such investigations.

3.2.4. *Optical rotation techniques*

If plane-polarized light is incident upon a magnetic surface, the reflected light is found to be elliptically polarized even if the incident light is polarized in one of the principal planes of incidence. The degree of ellipticity is small and the effect, known as the magnetic Kerr Effect (to distinguish it from the better known electrical effect), can be regarded as a rotation of the plane of polarization upon reflection. To a first approximation the rotation is proportional to the first power of the magnetization of the surface and so the effect can be used to study the domain structure of any reflecting surface. There are a number of difficulties, mostly connected with the smallness of the rotation and the consequent lack of contrast and definition. Unfortunately, too, the effect is greatest when the magnetization is normal to the surface, a state of affairs which rarely exists except in permanent magnet materials.

The technique was first successfully employed by Williams, Foster and Wood (1951) who viewed a cobalt surface between nearly crossed Nicol prisms and observed the domain pattern, both visually and with photographic techniques. Subsequently, Fowler and Fryer (1954a) developed the method to a high degree of sensitivity and precision but in order to obtain good contrast had to employ photographic techniques which they developed specially (Fowler and Fryer 1954b). So far the method has proved most successful with evaporated films (Fowler and Fryer 1955, Fowler *et al.* 1956), particularly those of 80/20 nickel-iron, in which the anisotropy is low and the domains may not be visible with colloid techniques. These films are usually metallurgically almost perfect and have a mirror-like surface which is ideal for this type of work. With films thin enough to be transparent domain patterns may be observed using the Faraday Effect (Fowler and Fryer 1956) but the definition so far obtained is rather less than that using reflected light. Definition may be improved by the use of an anti-reflection coating on the surface (Heinrich 1956), similar to that used in 'blooming' lenses.

A variation of this technique which appears to possess certain advantages over existing methods has been developed by Lee *et al.* (1958). In this method the surface is slowly scanned with a small probe of plane-polarized light. Domain walls are observed by applying a small alternating field to the specimen under investigation. When a domain wall moves across or within the probe the intensity of the reflected light varies at the same frequency as the applied field and this can be detected using a photomultiplier and amplifier. The advantage of this method is that surface imperfections do not obscure the domain walls since they contribute a steady change in the reflected light intensity, and this d.c. component of the signal can easily be removed. The method has been successfully used with

Perminvar and similar materials possessing a rectangular B/H loop though its definition is poor since this is limited by the finite size of the optical probe.

3.3. Magnetostriction

In common with all other even-power effects, the measurement of magnetostriction as well as magnetization is often capable of giving useful information regarding initial domain configuration and the magnetization processes (magnetoresistance measurements can provide similar information—Parker 1956). Magnetostriction relations in materials possessing preferred domain orientation have been discussed by Rado (1954). An example of a recent investigation with some crystals of 3% silicon-iron is provided by the work of Lee (1955). With materials of highest permeability the magnetostriction is often so small that special techniques have to be employed. For measurement of strains down to about 1.0×10^{-6} strain gauges provide the most convenient method but for strains smaller than this a better signal-to-noise ratio is obtainable with combined mechanical-electrical methods than with purely electrical ones. The difficulty in most cases is one of providing adequate thermal stability since even the smallest magnetostrictive strains are large compared with what is theoretically measurable.

For measurement of the actual magnetostriction constants the technique developed by Bozorth and Hamming (1953) sets a standard of accuracy which leaves little to be desired.

3.4. Magnetothermal Methods

If the magnetic field acting on a thermally isolated substance is increased by an amount ΔH it may be shown from thermodynamics that a resulting heat change occurs in the substance given by

$$\Delta Q = -T \left(\frac{\partial I}{\partial T} \right)_H \Delta H.$$

In ferromagnetic substances ΔQ may be quite large on account of the large value of dI/dT but below saturation this equation is often inapplicable because of irreversible magnetic changes and consequent irreversible heating produced by the application of the field ΔH . A detailed analysis of the effect by Teale and Rowlands (1957) shows that if a field H_1 acting on a ferromagnetic substance is increased to H_2 , thereby increasing its magnetization from I_1 to I_2 , the *reversible* component of the thermal change Q_R is given by

$$Q_R = a(H_1 I_1 - H_2 I_2) - c \int_{H_1}^{H_2} H dI_R$$

in which dI_R is the reversible increment of I . In this equation the first term represents the change in intrinsic magnetization and the second represents the change due to all other reversible magnetic changes. The constant c depends on the type of magnetization process (wall displacement,

rotation against crystal anisotropy, rotation against internal stresses, etc.) and can in principle be calculated for any of these. Consequently, measurements enabling c to be calculated and compared with the theoretical values can be used to decide what type of magnetization process is operative at any stage of magnetization. The real problem is to know just how reliable the theoretical estimates of c are, but in some cases the estimated values for different magnetic processes are so different that an unambiguous decision is possible from magnetothermal measurements (see e.g. the establishment of rotational processes in manganese-zinc ferrite by Bates *et al.* 1958). In really high-permeability alloys it would appear that the anticipated reversible thermal changes are too small to be measured with sufficient accuracy for accurate analysis.

3.5. Alternating-current Methods

Measurements in alternating fields may not disclose any phenomena not observable otherwise, but they are directly related to many conditions of practical use and they may be easier than measurements in static fields.

Wilde (1952) called attention to the advantages of mutual-inductance methods over self-inductance; they are (1) the 'iron' loss is measured without the 'copper' loss and (2) a very desirable form of bridge network can be used in which both oscillator and detector are connected to earth, so that the apparatus can be used over a large range of frequencies. Whether self or mutual inductors are used, their inductance should be kept small (Lynch 1955), so that the errors introduced by self-capacitance of windings, and by capacitance between two windings, are negligible; this is in any case convenient, since it implies the use of specimens of small cross section and having windings of only a few turns (e.g. a single ring of $1\frac{1}{2}$ in. outer diameter, 1 in. inner diameter, 0.004 in. thickness, carrying a 20-turn winding) (Richards *et al.* 1957).

Examples of bridges suitable for measurements at low flux densities over a wide range of frequencies are given by Welsby (1943), Wilde (1952), Epelboin (1952) and Lynch (1955). Welsby prefers resonance bridges, on which, however, a given specimen can be measured in only a restricted range of frequencies. The other authors recommend variants of what is essentially a Maxwell or an Owen bridge.

At frequencies too high for bridge methods (> 10 Mc/s according to Epelboin or Lynch) resonant-circuit methods are necessary. At frequencies up to about 100 Mc/s the apparatus comprises some form of resonance indicator used with a parallel-tuned circuit including at least one variable capacitor. At still higher frequencies coaxial-line and waveguide methods are used.

Unless the flux density is small, a distinction is necessary between measurements with sinusoidal fields and those with sinusoidal flux densities. The fact that these are not equivalent is easily seen: in large sinusoidal fields the flux density is near the saturation value, in one direction or the

other, for nearly the whole of the cycle; but there is no corresponding condition possible at high sinusoidal flux densities. Sinusoidal flux is usually the more important in practice, since it corresponds to sinusoidal applied voltage, but measurements in either condition are possible. The use of indefinite intermediate conditions should be avoided except when testing a material in some particular condition in which it will be used.

When the flux density is not small, the distortion introduced by the specimen may make the results of bridge or wattmeter measurements unreliable. The specimen may be thought of as converting energy from the fundamental frequency to harmonic frequencies, which will then escape reckoning in the balancing of a bridge or in the reading of a wattmeter. It is possible, however, to make corrections for the energy lost in this way (Cooter and Harris 1956). Two better although more complicated plans are: (1) to control the magnetizing current (by negative feedback from the specimen itself to the oscillator amplifier) in such a way that either the field or the flux in the specimen is sinusoidal (McFarlane and Harris 1958), (2) to add negative resistance in series with the specimen, balancing the positive resistance inevitably brought in by the specimen itself and the measuring apparatus, so leaving the specimen connected as if across a source having zero impedance (Cooter and Harris 1958). In either of these conditions the permeability and losses are truly measured even at high flux densities. In bridge methods there is a further practical difficulty, formidable though not insuperable, of balancing the fundamental frequency in the bridge in the presence of harmonics.

Before the controlled-waveform methods had been developed, thermal methods were used for the measurement of a.c. losses (Greig and Kayser 1948), and they remain the more suitable for the study of extreme cases of high flux densities (Brailsford and Bradshaw 1955). Normally they are slow to use, but one method has been described in which the experiment is completed in a few seconds (Bates *et al.* 1953).

Special apparatus based on the use of electronic gates has been used to measure the instantaneous rate of loss of energy at specific stages in the cycle (Aspden 1956).

3.6. Electropolishing

A question which frequently arises in connection with soft magnetic materials is that of magnetic inhomogeneity. This is usually assumed to take the form of a continuous variation of permeability from the surface of the specimen towards the centre, and the problem is, first, to establish the existence of inhomogeneities, and secondly to find the form of the variation $\mu = f(d)$. To achieve this the properties of the layers near the surface of a material can sometimes be deduced by etching these layers away chemically and testing the material which remains. An improvement in technique, allowing the controlled removal of very thin layers, is to use electropolishing instead. The electrolyte must be chosen to suit the particular alloy which is to be polished. A circuit allowing precise control of the polishing current has been described (Bates and Mee 1950).

Abadie and Epelboin (1948) succeeded in electropolishing a single surface of their specimens, so that by removing the majority of the material they could test the material which had originally formed a thin layer at the other surface.

§ 4. SOME NEW MATERIALS

Many minor variations in ferromagnetic alloys have been made in recent years; the alloys chosen for mention here are those which are, or may prove to be, of major technical importance. This section also includes a brief summary of the properties of evaporated-on metal films, which although not new materials, possess properties very different from those of materials in conventional forms.

4.1. *Iron-Aluminium* ('Alfer' or 'Alfenol')

Alloys of iron and aluminium have long been known to have interesting magnetic properties; Snoek (1947) mentions the existence of such alloys having zero anisotropy, and of a ternary alloy with silicon which has the anisotropy and the magnetostriction simultaneously zero. The ternary alloy has been produced in powder form in Japan and in Germany under the name of Sendust; but the alloys are difficult to work and did not come into general use as sheet, although they were produced in Japan during the war.

Nachman and Buehler (1954) have shown that the iron-aluminium alloys containing from 12 to 16% aluminium (by weight) can be mechanically worked within a limited range of temperatures, in which an ordered structure exists. (The ordered alloy is Fe_3Al , containing 13.9% Al.) By rolling at about 550°C they produced sheet of thicknesses down to 0.007 in. and they state that further rolling is possible without special precautions. The material is remarkable for its high resistivity (150 microhm-cm) and for the high permeability developed in the disordered state obtained by quenching— $\mu_{\text{max}} = 100\,000$, although $\mu_a = 4000$. It is less strain-sensitive than the nickel-irons having high permeability. The process for making the alloy seems, however, to be difficult enough to prevent it from coming into general use.

Hall (1958) gives data on the magnetostriction and anisotropy of single-crystal specimens in ordered and partially-disordered states, for compositions ranging from 0 to 30 atomic % of aluminium.

4.2. *Improved Iron-Cobalt* ('Supermendur')

The 50/50 iron-cobalt alloy has long been known to have a uniquely high maximum flux density, although it has not been so generally recognized that, because its coercivity is 2 oersted, its advantage over pure iron shows only at high fields. It is a difficult alloy to work, and its use has been further restricted by the price, high until recently, of cobalt.

The new feature of a process proposed by Gould and Wenny (1957) is that purification is completed in the melt instead of being left for completion in the final anneal. The subsequent heat-treatments can then be at temperatures below the α - γ transformation point at 850°C, and the resulting

crystal structures are such that the alloy does not become brittle, as it normally would. In any case they recommend rolling from 0.090 to less than 0.001 in. without intermediate anneals. An ordered structure is known to be possible in this alloy, but Gould and Wenny do not mention its rôle in their process.

The alloy can usefully be given a magnetic anneal. It then has $B_{\max} = 24\,000$ gauss, $B_{\text{rem}} = 21\,000$ gauss, $H_c = 0.26$ oersted, and $\mu_{\max} = 66\,000$. Gould and Wenny consider it to be a possible material for use in power transformers.

4.3. Cube-oriented Silicon-Iron

The grain-oriented silicon iron now available has a 'roof-top' structure in which one direction of easy magnetization lies along the rolling direction in the plane of the sheet but the others point out of it. Thus at right angles to the rolling direction magnetization is difficult, especially to values greater than $B_{\text{sat}}/\sqrt{2}$. Consequently, the advantages of the material—namely low hysteresis loss and the possibility of using it at very high flux-densities (a result of the rectangularity of its loop)—are realized only when it is magnetized along the rolling direction. This is inconvenient in small transformers and impossible in the stators of rotating machines.

Sixtus (1935) had observed an orientation component in 3% silicon-iron which he identified as (100) [001]; but it was not until the work of Assmus *et al.* (1957) that this component was made to grow by secondary recrystallization until it formed 90% of the whole—the first time that such a result had been obtained in a body-centred cubic magnetic material.

In 1957 two American groups (Walter *et al.* 1958, Wiener *et al.* 1958) simultaneously announced that they had made the desired material on a pilot scale, but neither has produced it for general use. No details of their processes are known, but the secret probably lies in a controlled degree of cold-rolling and the inclusion (and possibly the subsequent removal) of an impurity which governs the type of recrystallization in the final heat-treatment. The properties of the material can be summarized as follows:

	Along rolling direction		Across rolling direction	
	'Roof-top' material	'Cube' material	'Roof-top' material	'Cube' material
Maximum permeability	55000	116000	8000	65000
Coercivity, oersted	0.08	0.07	0.27	0.08
Remanence, gauss	9500	12200	1750	11500
Loss at 1500 gauss, 60 c/s, watts/lb†	0.60	0.56	1.60	0.65

† Strip thickness not stated but presumably 0.012 in.

4.4. *Evaporated-on Films*

In the last few years there has been intensive study of the properties of thin films, especially those of nickel-iron alloys deposited by evaporation. Most of this work is specifically directed towards the production of memory devices for computers, for which the desirable properties are a rectangular hysteresis loop and rapid switching in not too large a driving field. These requirements dominate nearly all the published work.

Most of the reported properties of thin films might have been predicted, although in fact observation has preceded explanation in nearly every respect. The films are ferromagnetic in thicknesses down to about 30 Å. They can be given rectangular loops by the presence of a magnetic field when they are deposited, or by heat-treatment in a field subsequently. Reported coercivities range from 1 to 300 Oe; the low values, while higher than those for bulk material, are in line with those for very thin rolled strip. Bozorth (1957) suggests that the high values result from imperfections in the films, and are therefore of no theoretical interest—although for the application to computers this wide range of values is a serious problem. A particularly troublesome effect is strain due to differential contraction of film and substrate during cooling; it is minimized by working with the composition (83% nickel) for which the large-field magnetostriction is zero.

Domain structures can exist in these films, and can be detected by Bitter figures (Williams *et al.* 1957) even when the composition corresponds to that for high permeability and therefore low anisotropy. Fowler and Fryer (1955, 1956) detected the domain structures by the Kerr effect, but only when the films were less than 10 000 Å thick. The domains are few (as the rectangularity of the hysteresis loop suggests) and identical patterns are found on the two faces of the film. The domain boundary usually consists of a series of parallel spikes. Fuller (1959) has studied the nucleation of domains, and found straight or spiky boundaries according to the angle between the magnetizing field and the easy direction in the film.

Reversal of magnetization in these films can, however, be a rotational process. Rotation can be encouraged by the application of a transverse field in addition to the main field which causes the reversal (Smith 1958); without the transverse field the magnetization might remain in a state of unstable equilibrium in the applied field, and even if it rotated at all the motion would begin very slowly. If this bias is applied, the rotational process is rapid—faster by a factor of at least 10 than reversal by wall movement because the whole of the material is responding simultaneously rather than small areas of it being affected in succession.

Observations of potentials induced in pick-up coils set in appropriate directions confirm that for the thinner films (2000 Å) the process is rotation in the plane of the film, not rotation about an axis in this plane (Bradley and Prutton 1959). The absence of Barkhausen discontinuities—which may appear in the absence of the transverse bias—confirms that the process is rotational. In thicker films, Bradley and Prutton believe several processes to occur simultaneously.

The first attempts to calculate the time required for reversal underestimated it seriously. Use of the correct expression for the damping (eqn. (8), p. 339) leads to the observed result, a few tens of millimicroseconds (Smith 1958).

§ 5. CHARACTERISTICS OF SOFT MAGNETIC MATERIALS

In this section we briefly review ideas and theories concerning various quantities such as initial permeability and coercive force which are important material characteristics.

5.1. Initial Permeability

In low fields the magnetic induction obeys a relation of the form

$$B = \mu_a H + b H^2.$$

The constant μ_a is the initial permeability and b is a constant. For pure polycrystalline iron μ_a is about 150 (Bozorth 1951). This can be increased to 14 000 by very careful purification by prolonged annealing in hydrogen (Cioffi 1934). The constant b is not independent of μ_a . Indeed, as a result of a comprehensive study of the initial magnetization curves, Kornetzki (1952, 1954, 1956) came to the conclusion that the relation

$$b/\mu_a = C(\mu_a - 1),$$

in which C is a constant, is obeyed fairly well by a large number of different materials ranging from permanent magnets to high-permeability alloys.

The measured initial permeability of a polycrystal is made up of a rotational permeability μ_R and a part due to domain wall displacements, $\mu_W \cdot \mu_R$ can be calculated easily if the nature of the restoring torque on the domain magnetization vector is known. In the absence of magnetic interactions it may be shown (Néel 1943) that for materials whose crystal structure is cubic

$$\mu_R = \frac{4\pi I_s^2}{3(K_1 + \lambda_s \sigma_1)} \dots \text{ if } K_1 > 0;$$

$$\mu_R = \frac{4\pi I_s^2}{2K_1 + \frac{3}{2}K_2 + 3\lambda_s \sigma_1} \dots \text{ if } K_1 < 0;$$

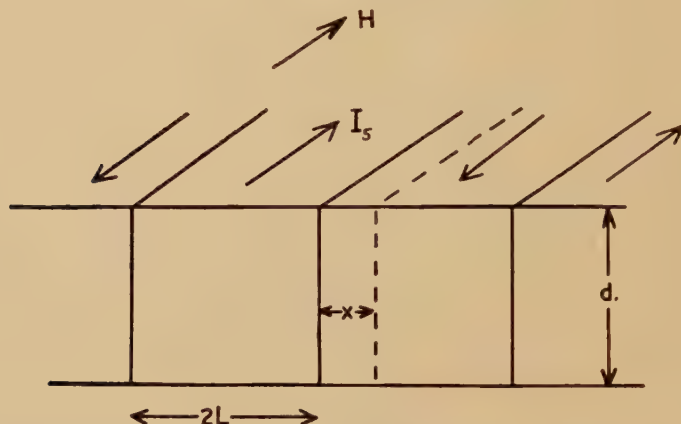
in which K_1 and K_2 are the first and second anisotropy constants, λ_s the isotropic magnetostriction constant and σ_1 the internal stress amplitude; in addition it has been assumed that $\mu_R \gg 1$. For uniaxial materials with a single easy axis μ_R is the same as when $K_1 > 0$. In ideal well-annealed material the only stresses are likely to be frozen-in magnetostrictive stresses which arise as the material is cooled through the Curie temperature. Under these circumstances σ_1 is of the order of $\lambda_s E$, where E is Young's modulus.

The boundary displacement permeability μ_W is a measure of the ease with which a domain boundary may be reversibly displaced from its position of equilibrium in zero field. It is convenient to discuss boundary

displacement permeability in terms of a simple model in which a ferromagnetic substance is uniformly divided by 180° walls as shown in fig. 1. Suppose $2L$ is the distance between adjacent 180° walls and α is the restoring force per unit area of wall per unit displacement. The pressure exerted by the field H on each wall is $2HI_s$; in consequence the wall is displaced a distance x , given by

$$2HI_s = \alpha x.$$

Fig. 1



Section through a simple domain model consisting of uniform array of 180° domains.

The change in magnetization is $2xI_s$ per wall. If there are N walls per cm, this becomes $2xI_sN$. The initial permeability is then $8\pi I_s^2/\alpha L$, assuming $\mu \gg 1$, in which we have made use of the fact that $N = \frac{1}{2}L$. If the material is divided by 90° or similar walls a different numerical factor is obtained but the form of the expression remains unaltered. This analysis, however naïve, has the great merit of showing very clearly the factors which any theory of initial permeability must take into account. Clearly the first problem is to seek a mechanism responsible for providing the restoring force α . It seems generally agreed that some form of lattice defect must be invoked. In general, the stress field around a defect will interact with the magnetostriction constant to give an energy term which is superimposed upon the anisotropy energy which makes the energy of the wall depend somewhat upon its position. Such stresses can arise at grain boundaries, dislocations, point defects, i.e. vacancies, and in alloys by precipitation of a second phase and possibly from the presence of short-range order.

The existence of point defects in ferromagnetic metals could, in principle, be established from a study of their magnetization curves near saturation but accurate measurements are very difficult to obtain. Precipitation when it occurs usually introduces very large stresses and frequently gives

rise to internal poles, since the spontaneous magnetization of the precipitated and matrix phases are in general different. Such materials often develop very high coercivities. The appropriate interaction energy is

$$E_{\sigma} = -\frac{3}{2}\lambda_{100}\sigma(\alpha_1^2\gamma_1^2 + \alpha_2^2\gamma_2^2 + \alpha_3^2\gamma_3^2) \\ - 3\lambda_{111}\sigma(\alpha_1\alpha_2\gamma_1\gamma_2 + \alpha_2\alpha_3\gamma_2\gamma_3 + \alpha_3\alpha_1\gamma_3\gamma_1)$$

in which σ is a linear stress and α_i and γ_i are respectively the direction cosines of I_s and σ with reference to the crystal axes, so that even if the type of defect responsible for the stress distribution is known a rigorous calculation of the energy E_{σ} is difficult; moreover a calculation of $\partial E_{\sigma}/\partial x$ must necessarily depend on the manner in which the defects are distributed throughout the material. Consequently the theories so far put forward have postulated a system of internal stresses enabling relatively straightforward calculations to be made, without enquiring very closely into the physical plausibility of the stress distribution actually assumed. The strain theories assume isotropic magnetostriction and give expressions for the coercivity (Kersten 1938), initial permeability (Kersten, 1931), the change of remanent magnetization with tension, the work of magnetization, the ΔE -effect (Becker and Döring 1939) and the approach to saturation (Becker and Polley 1940) in terms of an internal stress σ_i , and, in the case of the coercive force only, a numerical constant adjustable between 0 and 0.7. But when σ_i is calculated from each of these quantities, all measured for the same specimen, differing values are usually obtained (Köster 1948). Thus, the precise physical significance of the strain formulæ is very doubtful. They are nevertheless frequently very useful as a rough and ready guide to anticipated behaviour and can often be used to predict magnetic quantities to an order of magnitude.

In addition to the energy which arises from the interaction of the stress field around a defect with the magnetostriction, defects of the kind already mentioned, together with holes and non-magnetic impurities, will in general give rise to magnetostatic energy caused by non-zero divergence of the magnetization vector. A domain wall containing such defects may have a lower energy in one position than when it is in another and will effectively be bound to the position of lowest energy. Whether the inclusion is large enough to have closure domains associated with it or not, the energy problem is a magnetostatic one suitably modified by the μ^* effect (Williams *et al.* 1949). But the calculation of the restoring force requires knowledge of $\partial E/\partial x$ and this depends upon the manner in which the domain walls are deformed by an applied field.

Now the observations so far made do little more than show the extreme complication which the problem of a calculation of the initial permeability presents. Unfortunately these wall-impedance models all suffer from a further inherent objection apart from that of mathematical intractability, for when the restoring force α has been calculated the expression for μ_0 still contains L in the denominator. Now it is possible to vary the domain

size, L , in polycrystals by varying the grain size. Theoretical calculations by Martin (1957) for single crystals amply supported by experimental observations by Bloor and Martin (1959) on polycrystalline silicon-iron show that L decreases with decreasing grain size. Experimental studies of the variation of permeability with grain size in polycrystals are not as plentiful as may be desired but those that have been carried out show that, generally speaking, decreasing grain size is accompanied by a decreased initial susceptibility—never the reverse. Thus we are led to the conclusion that wall impedance due to imperfections within the wall itself can provide only a quite small contributory factor to the total wall impedance.

An alternative approach is to examine the extent to which domain walls may be held by closure domains formed at the surface of the crystal grains. This was first done by Kolodenco (1947) and further, more exact calculations have been carried out by Martin (1959, private communication) which give the right dependence of initial susceptibility with grain size.

Acting upon a suggestion of Bozorth (1953), Lee and Jackson (1958) examined the possibility that the domain wall restoring force is caused partly by effects of the type mentioned above and also by the stress set up by the magnetostrictive deformation associated with movement of a 90° wall. Using only the observed fact that in high permeability alloys the initial permeability decreases linearly with decreasing grain size (Walters 1955) they showed that an equation of the form

$$\mu_w = \frac{B_s^2}{cK^{1/2} + b\lambda e^2}$$

could be justified semi-theoretically and also fits the available data on disordered nickel-iron alloys. In this equation c and b are constants and λ_e the magnetostriction constant in the easy direction. The form of this equation closely resembles one obtained by Kersten (1956).

5.2. Maximum Permeability

It is improbable that a domain wall obeys Hooke's Law for finite displacements. Instead, the restoring force will be a much more general, and usually unknown, function of the displacement. A useful approximation is

$$F = \alpha x - \beta x^3$$

where α and β are positive constants. Then we have

$$2HI_s = \alpha x - \beta x^3.$$

The wall thus moves reversibly until a critical displacement x_0 is reached at which the restoring force reaches a turning point, i.e. when $\partial F/\partial x = 0$, namely when $x_0^2 = \alpha/3\beta$. It then moves irreversibly without further increase in field. This is the usual explanation of a Barkhausen jump. The critical field H_0 is given by

$$2H_0I_s = \alpha x_0 - \beta x_0^3,$$

i.e.

$$H_0 = \left(\frac{\alpha^3}{27\beta} \right)^{1/2} / 2I_s.$$

It thus depends upon a single parameter α^3/β . The irreversible change in magnetization however is $2XI_s$, where X is the distance the wall moves, irreversibly, before being halted by a greater impedance. If X were approximately the distance between adjacent domains, the magnetization curve, even allowing for some variation in H_0 , would be non-linear but reversible in low fields, and would have a number of Barkhausen discontinuities equal to the total number of domains. Experimentally, non-linearity in the initial magnetization curve is always accompanied by irreversibility, even at very low fields (Rayleigh's Law), and the measured size of a Barkhausen discontinuity always corresponds to a change of magnetization in a volume much less than that of a domain. Thus we are led to the conclusion that X is much less than the domain width. There is of course no reason why the whole wall should move through the same distance. Indeed, in a theoretical analysis of the Barkhausen Effect, Tebble (1955) came to the conclusion that the only process capable of producing discontinuities of the order of magnitude which is observed, and which will result in a magnetization curve of the usual shape, is one involving limited lengths of a 180° boundary and inclusions whose width is of the same order as the boundary thickness. For the moment we may expect that the critical field H_0 will be different for different domain walls or even for different parts of the same wall. We may also expect X to increase with increasing H_0 , subject of course to the restriction that X cannot be greater than the domain width $2L$. The problem therefore is to find the appropriate distribution function for H_0 and the relation between X and H_0 . This is once again almost impossibly complicated and we are unaware of attempts to solve it.

Nevertheless we can see in a general way how the parameters H_0 and X determine the shape of the magnetization curve. It seems unlikely that X could be independent of H . If it is simply proportional to H , we have the normal round-shouldered curve which is usually considered characteristic of ordinary materials. The hardness or softness of the material is then determined by H_0 . If on the other hand X increases rapidly with H , we obtain a deep-sided magnetization curve similar to that observed in single crystals magnetized along an easy axis.

5.3. Coercive Force

In soft magnetic materials magnetization is usually reversed by the creation and growth of domains of reverse magnetization. The coercive force is a measure of the critical field strength to initiate irreversible growth of reverse domains. No additional quantities enter into the calculations, the results of which are in consequence much more reliable than those of initial and maximum permeability. Reverse domains require nucleation and nuclei can in principle occur at all imperfections including the crystal surface. If there were no nucleating centres the observed coercive force would be several orders of magnitude greater than that which is actually

observed, a fact first pointed out by Brown (1945)[†]. This prediction has recently received rather striking experimental verification. Single crystal iron 'whiskers' of a high degree of crystallographic perfection were found (DeBlois and Bean 1959) to have a coercive force of 480 oersteds, in good agreement with the theoretical value $2K_1/I_s$, namely 510 oersteds, calculated by Brown. Goodenough (1954) has examined in detail the possible nucleating centres which might be operative in a random polycrystal. He concludes that the most likely nuclei are granular inclusions, if they are large enough, and lamellar discontinuities such as lamellar precipitates or grain boundaries. Both contribute to the coercive force which Goodenough calculates to be of the form

$$H_c = \frac{a\sigma_w}{I_s} + bI_s$$

in which a and b are constants and σ_w the wall energy. The first term represents the contribution due to granular inclusions and the second term, that due to grain boundaries. Since σ_w involves the total anisotropy $K + \lambda_s\sigma_1$, H_c will increase with increasing internal strain but this effect is quite separate from the contribution to H_c which may exist if there are local strains in the material. These will give rise to a coercive force which for moderate internal strains will probably be larger than any contribution arising from the mechanisms considered by Goodenough, and which may be calculated to a first approximation from the standard formulae developed from the strain theory of Becker and Kersten, or more accurately from Néel's (1947) formulae, viz.

$$H_c = \frac{4}{15\pi} \frac{fC^2}{KI_s} \left\{ 1.386 + \frac{1}{2} \log_e \left(\frac{2\pi I_s^2}{K} \right) \right\} \quad . \quad . \quad . \quad C/K \leq 1,$$

$$H_c = 0.69 \frac{fC}{I_s} \left\{ 1.386 + \frac{1}{2} \log_e \left(\frac{6.8 I_s^2}{C} \right) \right\} \quad . \quad . \quad . \quad C/K \geq 1,$$

in which C is the strain energy which affects a fractional volume f . Goodenough's analysis is based on the restriction that the inclusions are large enough to permit formation of reverse domains with themselves as nuclei. For very small inclusions it will be energetically favourable to avoid domain formation and to allow the existence of free poles. In these circumstances the formula of Néel (1947) applies, viz.

$$H_c = \frac{2K_1 f}{\pi I_m} \left\{ 0.38b + \frac{1}{2} \log_e \left(\frac{2\pi I_m^2}{K_1} \right) \right\}$$

in which f is the fractional volume of non-magnetic inclusions and I_m is the mean magnetization.

[†] In this connection it is perhaps worth pointing out that the iron specially purified by Cioffi, although possessing higher initial permeability than technically pure iron, also has a greater coercive force.

5.4. Remanence

The classical picture of the remanent state is that first given by Gans (1932). In this it is assumed that when a saturating field is reduced to zero the domain magnetization vectors in each crystal grain lie in the one easy direction which lies nearest the direction in which the field was applied. If there is no preferential orientation of crystal grains then this model requires that the remanence ratio should be 0.83 when the crystal structure is cubic and the cube edges are the easy directions ($K_1 > 0$), and 0.87 when the body diagonals are easy directions ($K_1 < 0$). The possible effect of the second anisotropy constant on the remanence does not appear to have been considered although Bozorth (1936) showed that for certain values of K_1 and K_2 the easy direction might be the crystallographic [110]. In this case it is easy to show that the remanence ratio should also be 0.83. In the case of a non-aligned polycrystalline material having uniaxial anisotropy the remanence is 0.5 if the single axis is an easy direction and is zero if it is a difficult direction (in which case the plane perpendicular to it becomes an easy plane).

It seems rather unlikely that the situation assumed by Gans could exist in soft magnetic materials. The existence of a single direction of magnetization within each crystallite is bound to give rise to free magnetic poles at the grain boundaries. These will give rise to internal demagnetizing fields with a large associated energy. It is much more likely that closure domains form at grain boundaries so as to reduce the internal stray fields as much as possible. If this does not occur the external field will have to overcome these stray fields and the material will no longer be soft. Lawton and Stewart (1950) have considered this situation and have calculated magnetization curves based on the assumption that at remanence the magnetization vectors in each crystal grain are so distributed among the three easy directions nearest the field direction that the mean magnetization in each crystal grain is the same throughout the material. On this view the remanence ratio is simply that which an isolated single crystal would have if it were magnetized in the difficult direction, namely $1/\sqrt{3}$ independent of the sign of the anisotropy constant. For materials having uniaxial anisotropy the ratio would be zero in both cases. Actually in soft magnetic materials which have an induced uniaxial anisotropy such as Perminvar (annealed without a magnetic field) the observed remanence is virtually zero.

Bozorth (1947) has pointed out that the remanence ratios for cubic anisotropy are often very low indeed—values as little as 0.1 having been observed in Supermalloy and 6% silicon-iron (Boothby and Williams—unpublished data, quoted by Bozorth 1947). Actually it is no longer certain that this is not in part due to the development of Perminvar characteristics. Bozorth's suggestion was that low remanence ratios might be explained in terms of internal self-demagnetizing effects, i.e. to the formation of domain walls between saturation and remanence. For materials having large I_s and low K_1 domains of reverse magnetization might form at remanence or just before it is reached, provided that there exist nuclei on which these

reverse domains may be formed. Direct evidence that this does occur in single crystals of 3% silicon-iron was obtained by Bates and Hart (1953) using the powder pattern technique. Indirect evidence comes from analysis of magnetothermal investigations such as those of Bates *et al.* (1957).

5.5. Domain Structure

Most of our knowledge of ferromagnetic domains stems from fundamental studies using the magnetic colloid technique. Unfortunately the method fails for the nearly isotropic crystals of which very high permeability materials are comprised, owing to the fact that the surface fields are much weaker. Consequently our knowledge of domains in soft magnetic materials, particularly the high permeability nickel-iron alloys is not very precise.

The domain structure of any material is determined roughly by the requirement that the reduction in magnetostatic energy should exceed the increase in energy due to wall formation.

The wall energy is given approximately by

$$\sigma_w = c\sqrt{[A(K_1 + \lambda_s\sigma_1)]}$$

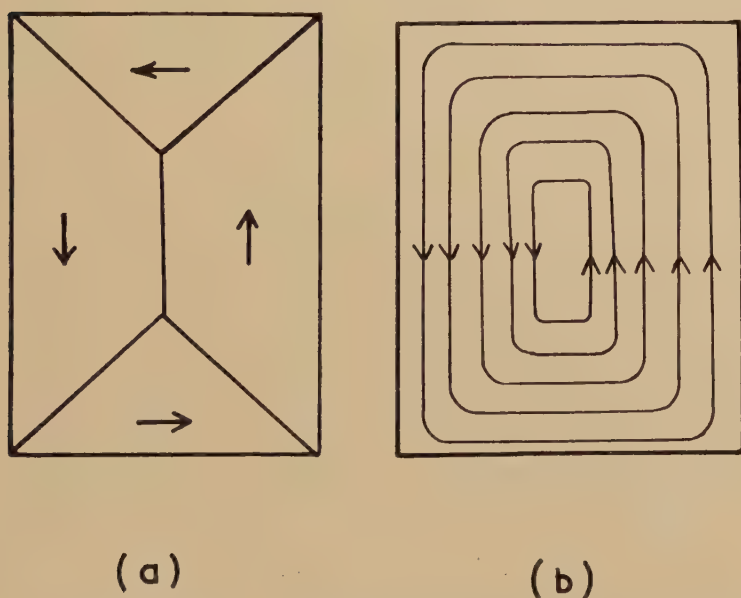
where c is a constant depending somewhat on the nature of the wall and A is the exchange energy density. Since A is approximately constant for all magnetic materials (it must be of the order kT_c) σ_w is determined mainly by the magnitude of the total anisotropy. The wall thickness is

$$\delta = d\sqrt{[A/(K_1 + \lambda_s\sigma_1)]}$$

in which d is a constant. Exact expressions for wall energies and thicknesses have been given by Néel (1944 c) and Lilley (1950) but precise numerical estimates for them cannot be given since one of the basic but largely unsolved problems of ferromagnetism is to know how to relate the exchange energy A to measured quantities. Rough estimates indicate that in cobalt δ is about 0.1 microns. In soft magnetic materials, in which K_1 may be only a few hundred ergs/cm², δ may be one or two microns. High-permeability materials are very often used in the form of laminations which have been rolled to a thickness of only a few microns. Consequently the wall thickness may be comparable in magnitude with the lamination thickness and often also with the grain size. In such circumstances the domain structure is likely to differ appreciably from that which would be observed on bulk material and is probably determined more by the requirements that the magnetostatic energy due to surface fields should be a minimum than anything else. Lee (1958) showed that the observed eddy-current loss in thin sheets of 77/14/5/4 nickel-iron-copper-molybdenum is consistent with the view that each crystal grain contains about four domains. A simple prismatic domain structure such as that shown in fig. 2(a) is suggested. The grain size in the material quoted is about 30 microns. Consequently each wall is about 1/20 the width of the complete crystal grain. Coupled with the fact that the free pole density at the grain boundaries must be minute (otherwise the permeability would

be very much less than the observed value of 4×10^4) it is evident that this type of structure is not essentially different from that first proposed by Kittel (1949) (fig. 2(b)) or from the idea of the closed flux shell suggested by Martius (1952). In this type of domain structure the magnetization must lie in the plane of the sheet or surface poles will be formed. This cannot happen readily unless the anisotropy is very small. Furthermore magnetization must take place by an intimate mixture of boundary displacements and rotations. This means that the very high permeabilities found in relatively thick laminations are not likely to be retained as the thickness is reduced unless the crystal anisotropy is vanishingly small. In other words a material which has high permeability on account of its low magnetostriction may have a progressively lower permeability as its thickness is reduced.

Fig. 2



Possible domain structures in very high-permeability materials: (a) is that suggested by the interpretation of eddy current losses (Lee 1958); (b) is that suggested by Kittel (1949).

Theoretical studies of ferromagnetic domains have largely been dominated by the requirement that no magnetic poles be formed on the domain boundary. The reason, first stressed by Néel (1944 a, b, c) is that if sheets of poles are allowed to appear large energies will arise owing to the field they produce. Domain boundaries can exist in which magnetic poles are not formed if $\text{div } \mathbf{I} = 0$ and this condition can be met if the normal component of the magnetization is continuous across the boundary. Such boundaries will have lower energy than those in which this is not so and in consequence may be expected to be more common. In general

quite small pole densities will give rise to energies which are appreciable in comparison with the anisotropy and exchange energies. In consequence existing theoretical treatments regard the condition that $\text{div } \mathbf{l} = 0$ as the over-riding one and consider only those types of wall which satisfy this requirement. As a result the circumstances in which walls which contain free poles may be energetically favourable are not known. Néel (1955) has shown that in thin films the magnetostatic energy which arises from the component of \mathbf{l} at the intersection of a domain boundary with the surface may be very high, sufficient to increase the wall energy by a factor of 17. In very thin films (less than 100 Å according to Néel) a different type of wall in which spins remain in the plane of the film becomes energetically more favourable. However, on films much thicker than this there is ample evidence of 180° domain boundaries of a quite different type in which the boundary is not parallel to the direction of magnetization in the two domains which it separates (Williams and Sherwood 1957). In these circumstances some free poles must be formed and it seems likely that the wall energy and thickness is determined by the exchange and magnetostatic energies rather than the more usual balance between exchange and anisotropy energies.

In single-crystal whiskers of iron, of the order of 100 microns square and 1 cm long, Coleman and Scott (1958) found generally simple domain structures, but also some domain walls in 'forbidden' directions, such that the component of magnetization normal to the wall was not continuous. They also suspected that domain walls existed which attracted little or no colloid. DeBlois and Graham (1958) carried out similar experiments and showed that the 'forbidden' walls were intersections, in the plane of the surface, between two walls inclined at an angle such as 90°; they were in fact a feature, hitherto unobserved, of the closure-domain structure predicted by Landau and Lifshitz. Walls of this type may not attract colloid.

Huber *et al.* (1958) observed domain walls crossed at irregular intervals by short walls, which they called 'cross-ties', each ending abruptly with no closure structure. They interpreted this structure as the result of reversal, at intervals along the length of the main wall, of the direction in which the spins diverge from those of the neighbouring domain. At each reversal a cross-tie forms, between areas which belong to the same domain but in which the magnetic axes, close to the wall, are slightly different.

§ 6. THE PERMALLOY PROBLEM

6.1. *Statement of the Problem*

The Permalloy Problem is, says Bozorth, to explain the characteristic magnetic properties possessed by the binary nickel-iron alloys containing 35 to 100% nickel†. In particular, some explanation is needed for the very high initial permeabilities which can be obtained, by appropriate heat-treatment, in alloys containing about 80% nickel, and for the narrowness

† 'Permalloy' is a proprietary name which is used for nickel-iron alloys, not necessarily binary, in the whole of this range.

of the range of compositions which yields these results. An extension of the problem is that certain commonly used ternary and quaternary alloys have similar or better properties, but only if given a heat-treatment which gives poor results with the binary alloys (Bozorth 1951, p. 137); these alloys contain molybdenum and sometimes copper, and for any particular content of these additives there is only one ratio of nickel to iron which will yield the high permeabilities.

6.2. *Effects of Heat-treatment*

The heat-treatment of these alloys is now known to serve two different purposes: first, purification by prolonged heating at a high temperature; second, by cooling at a suitable rate or by 'baking' at a critical temperature, the production of disorder or of a controlled degree of ordering in the alloy.

Purification is an essential. It may be largely achieved at the melting stage, but most alloys benefit by a final treatment at say 1050°C for an hour or more, while the recommended process for Supermalloy includes a final treatment at 1300°C. In alloys which have never been melted, and which therefore need extra purification later, long times or high temperatures are equally effective (Richards *et al.* 1957). This evidence shows that there is no question here of precise temperatures or rates of cooling, but simply of a slow chemical reaction. The impurities removed are probably carbon, oxygen, and silicon, in quantities so small that they are scarcely detectable chemically.

Most of the very-high-permeability alloys mentioned above have nickel/iron ratios which are roughly in the proportion three to one. They may thus be regarded as alloys whose composition is close to Ni_3Fe with minor additions of third and fourth elements. The alloy Ni_3Fe shows marked ordering tendencies with a well-defined critical temperature at 490°C. Ordering is not however confined to this simple composition but is observed over a very wide range, from about 40 to 80% nickel (Wakelin and Yates 1953). Ordering also occurs in ternary and quaternary alloys.

6.3. *Conditions for Small Magnetostriction and Small Anisotropy*

The solution to the Permalloy Problem is, in brief, that high permeabilities are the result of satisfying two simultaneous conditions: small magnetostriction and small anisotropy. The magnetostriction relevant to initial permeability is that measured in the direction of easiest magnetization; in higher fields it is a combination of those in the easy and difficult directions. Grabbe (1940) showed that these two conditions are roughly satisfied in 79/21 nickel-iron which has been quenched from a temperature above 600°C—i.e. which is disordered. Bozorth and Hamming (1953) and Bozorth and Walker (1953) confirmed these results and showed that slow cooling, which produces partial ordering, leads to serious departure from both conditions. The more the ordering, the greater are both the magnetostriction and the anisotropy; so any treatment other than the quench is unsatisfactory. Bozorth (1953) discusses the properties of the binary alloys in detail.

In the ternary and quaternary alloys, however, the quench is found to be undesirable; there is an optimum rate of cooling which, for certain commercially-used alloys, is about 50 deg/hr at temperatures near 500°C (Bozorth 1951, p. 137). (The optimum rate would probably be different for other alloys.) There are no full data for these alloys but it seems likely that the magnetostriction and anisotropy become nearly zero when the alloy is slightly ordered and that one or both of them become larger when the alloy is either disordered or well ordered. Certain ternary and quaternary alloys, given their best heat-treatment, approach the required conditions more nearly than can any binary alloy. One such alloy is Superalloy (which contains 5% molybdenum) (Boothby and Bozorth 1947). Assmus and Pfeiffer (1953) showed that similar heat-treatment was effective on a range of quaternary alloys containing molybdenum and copper, and Walters (1956) showed the relation between the heat-treatment of one such alloy and its state of ordering.

The solution of the problem, as set out above, was made more difficult by false clues discovered by Wakelin and Yates and by Assmus and Pfeiffer, both of whom carried out thorough investigations and were unlucky in some of their findings. The former concluded that the ordering process in nickel-iron is so slow that it could not be significant in any commercial annealing process; the answer appears to be that the resistivity, which they took as the criterion of order, depends on long-range order, while the magnetostriction and the anisotropy depend on short-range order; so, as ordering proceeds, the magnetic properties rapidly reach their 'ordered' values while the resistivity does so only slowly. Assmus and Pfeiffer found that their quaternary alloys, when cooled at the rate giving the highest permeabilities, had a higher resistivity than when quenched. This, they thought, was inconsistent with ordering of the alloys. Lifshitz and Ravdel (1953), however, showed that these alloys, if containing more than 1½% of molybdenum, have a higher resistivity when ordered than when disordered†; they ascribed this effect to 'segregation' of molybdenum, but Jackson (1958) pointed out that it might well be the result merely of different band-structures of the metal in its ordered and disordered states.

6.4. *Magnetization Processes in High-permeability Alloys*

Although it is clear that high initial permeability results from the combination of low magnetostriction and anisotropy, and not to any great extent from either separately, it is not so clear why this should be so.

In alloys in which the anisotropy is very small, rotational processes become easier relative to wall movements, while the domain walls become wide and in principle could become comparable in size with the domains themselves, so that the domain structure would no longer exist. No observations of domains in high-permeability alloys have yet been possible, except

† Other examples of this behaviour are now known, notably Au_3Cu (Hirabayashi 1951) which however becomes normal at liquid helium temperatures (Sato 1957).

in thin films; Lee's (1958) interpretation of a.c. loss measurements, however, suggests the existence of domains whose thickness is of the order of 20 microns, while the thickness of the walls might be about 1 micron. The possibility therefore exists that high permeabilities are associated with either rotations or domain wall movements; and the domain walls might or might not be 180° walls. These arguments lead, for the initial permeability, to formulae of the type given in § 5.1.

The equation predicts high permeability when the anisotropy is small. It is doubtful, however, whether the anisotropy can become zero; the first coefficient, K_1 , can certainly do so, but K_2 probably does not vanish at the same time. Values for quenched binary alloys include the following (read from a graph) (Bozorth 1951, p. 571):

% nickel in alloy:	65	70	75	70	85
K_1 , ergs/cm ³ :	6000	3500	500	-3000	-7000

But K_2 is of the order of $-20\,000$ ergs/cm³.

There are no comparable data for ternary and quaternary alloys, but the general trend is likely to be similar. There is no combination of K_1 and K_2 , other than $K_1 = K_2 = 0$, which allows unhindered rotation into any arbitrarily chosen direction. For the small rotations associated with the initial permeability, there would be unhindered rotation if K_1 were negative and $K_2 = -3K_1$; but the available data do not suggest that this occurs in any known nickel-iron alloy.

In the range in which K_2 is negative and $|K_2| \gg |K_1|$, both the $[100]$ and $[111]$ directions are easy and unusual types of domain wall are possible. A 180° wall would tend to divide itself into four walls with appreciable spacing, so that its total thickness would be much greater than that calculated by the usual formula.

Bozorth points out that λ_{100} also passes through a zero at approximately 45% nickel, for which $[100]$ is the easy direction, and that the curve of initial permeability against composition shows a subsidiary maximum in this region. This curve as usually drawn, however, seems to refer to material of ordinary commercial quality, and higher permeabilities have been observed in material subjected to special purification. Williams, for example, found a value of 12 000, four times that shown on the traditional curve (unpublished data quoted by Bozorth 1951, p. 123). There are not enough data for various compositions to allow re-drawing of this curve using the values for well-purified material. Presumably the subsidiary maximum would remain, as there is no reason to expect the further purification to be any less effective for the 45% alloy than for its neighbours, but Williams's four-fold improvement is so remarkable that some further data to verify the shape of the curve would be welcome.

Certain observed data ought to help to decide which of the possible processes of magnetization actually occur in the high-permeability alloys.

The enormous increase in permeability produced by purification suggests that domain-wall movements are facilitated by the removal of inclusions and inhomogeneities capable of anchoring a wall. The reversible permeability at remanence is known to be nearly equal to the initial permeability (Jackson *et al.* 1958); this probably rules out 180° walls as making any great contribution to high initial permeability. Further, low magnetostriction alone is not a sufficient condition for high permeability: this suggests either that the process must be rotational, or that the rôle of distorted domain walls near spikes is important.

The evidence is thus inconclusive. The answer may become clearer if improved techniques of observation of domain patterns can be applied to alloys of high permeability:

§ 7. MAGNETIC ANNEALING AND RELATED TOPICS

7.1. *Abnormal Shapes of Hysteresis Loop*

The shape of the hysteresis loop of iron is so familiar that it is often believed to be representative of all materials. In fact hysteresis loops of a variety of shapes have been reported. Some of them arise from peculiarities (intentional or not) of the measuring circuit, but others certainly represent unusual properties of the specimens.

Stewart (1951) obtained a re-entrant loop† in direct-current conditions by arranging to reduce the applied field automatically as soon as a change of flux was produced. The interpretation of such loops is that the domain walls have a few positions of stable equilibrium, and require appreciable energy to pass from one to another; but they will usually have enough energy, if they are able to pass one barrier, to pass others as well. If the field is reduced when a wall starts to move irreversibly it will be stable in a new position. The effect will be observable only if there are few walls present—i.e. if the material normally shows a rectangular loop. These re-entrant loops cannot be observed with ordinary d.c. apparatus, but sometimes appear in a.c. conditions. One type of loop sometimes seen for magnetically annealed 65/35 nickel-iron includes short horizontal beak-like projections in the second and fourth quadrants (Morgan 1958): this must be the result of a temporary decrease in the driving field as the flux in the specimen begins to change, thus accidentally reproducing the conditions of Stewart's experiment. Loops for 50/50 nickel-iron have been published in which about half the nearly vertical part of the loop has a reversed slope; this is difficult to account for.

Certain changes in loop shape, observed when the loop is repeatedly traversed, are referred to in § 9.4.

Of rather greater importance are the constricted and rectangular hysteresis loops exhibited by a large group of alloys including the Perminvars. Constricted loops are observed in fairly small fields only, and have been known since 1921. If a saturating field is applied the loop

† One of which dB/dH is negative at certain parts of the loop.

shape becomes normal and the constriction re-appears only after the material has been re-heated above its Curie point. Both types of loop are believed to be fairly well understood in terms of magnetic annealing, which we next discuss in greater detail.

7.2. Results of Magnetic Annealing

It has been known for a long time that the magnetic properties of certain alloys can be affected to a remarkable degree by allowing them to cool from a high temperature in the presence of a magnetic field. This effect seems to have been first discovered by Kato and Takei (1933) who observed it in cobalt ferrite, although priority is often given to Kelsall (1934) who studied the phenomenon in a large number of binary nickel-iron alloys. The effect of this so-called magnetic anneal is to promote a remarkable degree of rectangularity to the hysteresis loop when measured along the direction of the annealing field. Measurements at right angles to this direction reveal an almost rectilinear loop of small slope and small area. These observations point to the existence of an induced uniaxial anisotropy with easy axis parallel to the annealing field.

The domain structure in magnetically annealed materials is in consequence rather simpler than that found in isotropic materials and consists very largely of parallel and antiparallel domains separated by 180° walls lying parallel to the direction of the annealing field. Evidence for this comes directly from the powder pattern investigations of Williams and Goertz (1952) and indirectly from magnetostriction investigations of Williams *et al.* (1941).

The experimental investigations may be divided into two classes: those dealing with the square-loop characteristics and those dealing with the anisotropy itself. The former are by far the more numerous. They show that magnetic annealing occurs in a large range of binary and ternary alloys but not in simple metals. However, the significant fact, apparently overlooked by most investigators, is that those alloys which respond to a magnetic anneal also possess unusually shaped hysteresis loops (a very full account is given by Kühlewein 1931) when annealed in the absence of a magnetic field. Fundamental investigations into the uniaxial anisotropy itself were lacking until the comprehensive investigations of Chikazumi on a series of binary alloys of iron and nickel. First the magnitude of the anisotropy was established (Chikazumi and Oomura 1955) and its dependence upon composition and rate of cooling. Previous work (Chikazumi 1950 a, b) had suggested a relaxation time for the development of the anisotropy strongly suggestive of a mechanism of atomic migration. Further investigation showed that magnetic annealing is effective in a single crystal of Ni_3Fe and established the true nature of the anisotropy, namely that the effect of the magnetic anneal is to superimpose, on the normal magneto-crystalline anisotropy, a uniaxial anisotropy with an energy minimum lying close to, but not in general coincident with, the direction of the annealing field.

7.3. *Earlier Theories*

The original explanation put forward to account for these effects was that given by Bozorth and Dillinger (1935). In this theory it was assumed that the anisotropy was induced by relief of magnetostrictive stresses by plastic flow at high temperature. But this mechanism, although it must be present, can account for only a small fraction of the induced anisotropy. In particular, on this hypothesis the induced anisotropy should be zero for alloys having zero magnetostriction at the temperature at which stress relief takes place. A more recent explanation due to Kaya (1953) required precipitation of Ni_3Fe as a separate phase in the form of prolate ellipsoids, the direction of whose long axes may be predisposed by the annealing field. It will be recognized that this is similar to a current explanation of high coercivity in permanent-magnet alloys. No explanation as to why precipitation of Ni_3Fe does not lead to high coercivity was put forward. In any case, apart from the lack of metallurgical evidence for precipitation of Ni_3Fe this explanation cannot explain how magnetic annealing is effective in a Ni_3Fe crystal.

7.4. *The Néel-Taniguchi Theory*

Actually Chikazumi's experiments are so complete as almost to suggest their own explanation and it is hardly surprising that a theory of these effects was proposed simultaneously by Taniguchi and Yamamoto (1954) and by Néel (1954). The basic idea behind both theories is the same and operates through the preferential distribution of unlike atom pairs. The coupling energy between an atom and its nearest neighbours may be expressed quite formally in a series of dipolar and quadrupolar terms. In a cubic crystal the anisotropy comes solely from the latter, the dipole terms contributing only the magnetostriction. In a substitutional alloy AB the three interactions A-A, B-B and A-B, which may be characterized by dipolar coupling constants C_{AA} , C_{BB} and C_{AB} respectively, may be expected to be different. The dipole energy between parallel dipoles on two neighbouring atoms, each possessing the same moment μ is

$$\frac{C_{ij}\mu^2}{r^2}(1 - 3\cos^2\phi)$$

where r is the distance between the two atoms and ϕ is the angle between the dipole moments and the line joining their centres. The total energy of an atom is thus

$$\sum \frac{C_{ij}\mu^2}{r^3}(1 - 3\cos^2\phi)$$

where the summation is over all nearest neighbours. The presence of a magnetic field determines ϕ and at the relatively high temperatures at which magnetic annealing is effective the crystal anisotropy must be such that $\phi = 0$, or at least very nearly so. However the coupling energy between one atom and its nearest neighbours may be still further reduced by a change in the number of A-B interactions. Interchanging a pair of atoms A and B

has the effect of increasing the number of A-A and B-B interactions by unity whilst reducing the number of A-B interactions by two. Everything thus depends on the magnitude and sign of a single parameter

$$C = C_{AA} + C_{BB} - 2C_{AB} \quad (1)$$

In any case the coupling energy may be decreased if the temperature is high enough to permit atomic migration. The effect of the magnetic anneal is thus to promote a kind of atomic ordering. However, the ordered structure thus produced is quite different from a normal superlattice since the symmetry of the two structures is quite different. Indeed the two types of ordering will in general be mutually exclusive. In this connection it is interesting to recall the observations of Snoek and Smit (cited by Rathenau 1953) that an alloy of composition Ni_3Fe exhibits no induced anisotropy by magnetic annealing if it is first put in the completely ordered state.

The treatments of Néel (1955) and Taniguchi (1955) are developed along slightly different lines and are indeed complementary to one another. Both show that this (magnetic) ordered structure gives rise to a uniaxial anisotropy superimposed on the normal crystal anisotropy (which must presumably be slightly altered by the process). According to Taniguchi the induced anisotropy has a complicated angular dependence but in certain special cases takes a simpler form. In particular the induced anisotropy in the (110) or (001) plane caused by a field applied along the [111], [110] or [001] directions is of the form

$$E = -K_a \cos^2 \theta$$

where

$$K_a = \frac{ANn^2C^2I_s^2(T)I_s^2(T')}{I_s^4(0)kT'} \quad (2)$$

in which N is the number of atoms per unit volume, n is the concentration of solute atoms and $I_s(T)$ and $I_s(T')$ are the values of the spontaneous magnetization at the temperature of measurement and at the temperature of magnetic anneal, C is given by eqn. (1), and A is a numerical constant having the values given in the following table.

Values of A for Various Cubic Lattices

Plane	Axis	f.c.c.	b.c.c.	s.c.
(110)	[111]	9	8	0
	[110]	27, 4	4	9, 2
	[001]	9, 2	0	9
(001)	[100]	9	8	0
	[100]	9, 2	0	9

In the general case the position of the energy minimum of the induced anisotropy does not coincide with that of the annealing field, a feature observed experimentally by Chikazumi (1956). Equation (2) indicates that

the effectiveness of a magnetic anneal is greater when the Curie temperature is high, since, although the temperatures at which atomic migration occurs are much the same for all ferromagnetic alloys, the tendency to order increases according to the saturation moment at that temperature. This is perhaps one reason why ternary alloys containing a fairly large percentage of cobalt (e.g. Perminvar: 45% Ni, 30% Fe, 25% Co) respond so well to a magnetic anneal. The values of A given in the table show that in the case of a random polycrystal the induced anisotropy is greater for an alloy whose crystal structure is f.c.c. than b.c.c. This is in agreement with experimental results.

It thus appears that magnetic ordering of this type should occur in all alloys provided their Curie temperature corresponds to an activation energy greater than that required for atomic migration. Whether the effect is sufficient to make a significant change in magnetic behaviour depends on the magnitude of the induced anisotropy in comparison with the normal crystal anisotropy.

Certain ferrites, notably those containing cobalt ferrite, also respond to magnetic annealing. They also exhibit 'Perminvar characteristics' in the ordinary annealed state. The idea that the mechanism responsible for the effect is the same as that for metals was put forward by Néel (1954), Taniguchi and Yamamoto (1956) and developed in detail by Taniguchi (1957). Although the precipitation theory has recently been revived as being applicable to cobalt ferrite by Williams *et al.* (1956) there seems little reason to doubt that the mechanism of atomic ordering is that which actually occurs. This conclusion is also confirmed by recent work by Wijn *et al.* (1957).

If an alloy is cooled slowly without a magnetic field, magnetic ordering can still occur within a single domain and even within a domain wall. This effect was first recognized by Taniguchi (1956) who showed that a domain wall is then subject to a restoring force which is large and approximately constant for displacements small compared with the width of the wall and which decreases rapidly for larger displacements. By considering different types of domain wall Taniguchi was able to show that most of the so-called 'Perminvar characteristics' (i.e. constant initial permeability in fields up to about 1 oersted, constricted B/H loop shape) obtained with certain annealed alloys, could be explained in terms of this domain wall stabilization.

The Néel-Taniguchi theory of magnetic annealing successfully accounts for a number of hitherto unexplained characteristics of ferromagnetic alloys. In the first place, it explains why the alloys which can be magnetically annealed are just those which exhibit the Perminvar characteristics of constricted hysteresis loops. Both phenomena are seen to be due to magnetic ordering, the former along a direction determined by an external magnetic field, the latter along directions fixed by the directions of magnetization within a domain and a domain wall. These directions may themselves be determined by the microstructure of the material. Secondly, the observation that constricted loops occur only when weak fields are used may be understood since the unusual loop shapes arise from the displacement of

domain walls from positions in which they have been stabilized by magnetic ordering. When a saturating field is reduced and a small reverse field is applied domains of reverse magnetization are formed at nucleating centres which will not, in general coincide with the positions where the original walls were stabilized. The loop shape is thus normal. Even demagnetizing by a diminishing alternating field will not necessarily re-create domain walls in their original stabilized positions. Slow cooling from above the Curie temperature is necessary to restore the constricted loop. Quenching from the same temperature prevents the development of magnetic ordering and after this treatment the hysteresis loops should always exhibit the usual shape, as is observed experimentally.

The theory also makes sense of a rather puzzling fact, namely that nickel-iron alloys in the range 40–65% Ni possess a smaller initial permeability after slow annealing than after quenching in spite of the fact that annealing decreases both the crystal anisotropy and magnetostriction due to an increase of lattice order (Bozorth 1953). The explanation seems to be that although the normal crystal anisotropy is reduced by lattice ordering, domain wall stabilization also takes place and this effect far outweighs the former. This fact is of great significance in understanding the Supermalloy problem (see § 6) for it implies that no alloy can possess a very high initial permeability after annealing unless its Curie temperature is sufficiently low to ensure that domain wall stabilization cannot take place. The reduction in Curie temperature is usually brought about in practice by small additions of molybdenum.

Although we have discussed the Néel-Taniguchi theory in an air of finality it is only fair to point out that the theory does not seem to be universally accepted. The objections seem to be based on certain experimental observations: evaporated magnetic films exhibit a uniaxial anisotropy if deposited in the presence of a magnetic field. With nickel-iron films this is to be expected on the basis of magnetic ordering but films of pure iron also exhibit the same effect. The question of purity is clearly of great importance here because quite small amounts of impurity may be sufficient to take part in magnetic ordering and thereby give rise to all the effects encountered with binary alloys. It has been reported (unpublished data quoted by Burbank and Heidenreich 1959) that the response of certain nickel-iron alloys to a magnetic anneal is greatly dependent upon the amount of oxygen present in the metal; alloys containing less than $10^{-4}\%$ oxygen do not respond at all to the treatment. Whether the oxygen promotes magnetic ordering or itself takes part in the ordering is not at present known. The behaviour of the evaporated iron films suggest the latter, but the mechanism is at present unknown.

7.5. *Anisotropy Induced by Cold-rolling*

In certain binary alloys a rectangular hysteresis loop may be induced by cold-rolling. This is due to the development of a uniaxial anisotropy and it was shown by Chikazumi and Oomura (1955) to be similar in origin to

that due to magnetic annealing. Its magnitude is however usually considerably greater. The effect is distinct from the mere production of rolling and crystallization textures, which however may be present as well. The theory was first given by Néel (1954) using the idea that atomic rearrangement of the same type as that involved in magnetic annealing, can be induced at low temperatures by mechanical deformation. The effect has recently been studied in detail by Chikazumi *et al.* (1957) using single crystal and polycrystalline Ni_3Fe , who were able to correlate the appearance of the induced anisotropy and its dependence on the degree of cold reduction, with the known mechanism of slip in f.c.c. alloys (see also Chikazumi 1958).

§ 8. FERRIMAGNETISM AND FERRITES

8.1. *Types of Ferrimagnetic Materials*

Some materials, including many compounds of ferric oxide, are such that, within each unit cell of the lattice, certain of the ionic magnetic moments are aligned in opposition to the others; this condition was named 'ferrimagnetism' by Néel. It may even happen that the moments aligned in one direction are exactly cancelled by those in the other: Néel called this 'antiferromagnetism', and it has been detected in a number of oxides and sulphides. In ferrimagnetics the observable magnetic moment, since it arises from a difference, tends to be low compared with that of an ordinary ferromagnetic.

At least four main groups of ferrimagnetic compounds are now known; these are the following:

Crystal system	Type of crystal	General formula
cubic	spinel	$\text{XO} \cdot \text{Fe}_2\text{O}_3$
hexagonal	magnetoplumbite	$\text{XO} \cdot 6\text{Fe}_2\text{O}_3$ and others
cubic	garnet	$3\text{M}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$
cubic	perovskite	$\text{M}_2\text{O}_3 \cdot 5\text{Fe}_2\text{O}_3$

In the formulae given in this table M is a trivalent rare-earth ion; X is normally a divalent ion but may be replaced by combinations of others—e.g. in lithium ferrite $\text{Li}_{1/2}\text{Fe}_{1/2}\text{O} \cdot \text{Fe}_2\text{O}_3$ or in γ -ferric-oxide in which each three divalent ions are replaced by two trivalent Fe ions and one vacant site in the lattice.

Many such compounds are still ferrimagnetic if Fe is replaced by Al, Mn or Cr. Variations from stoichiometry occur readily. Further, within any one of the four groups, solid solutions can be formed in any proportions, so that the total range of possible compounds is enormous.

The name 'ferrite' is applied to the spinels and sometimes to the other groups as well. It is a misnomer for all of them, since they are compounds of ferric, not ferrous, iron.

Other ferrimagnetic compounds have been reported by Jonker (1954, 1956), by Bertaut and Forrat (1958), and by Goodenough *et al.* (1958). Whether these are magnetically hard or soft has not been stated.

8.1.1. *Spinel-type compounds*

The spinel-type ferrites are described in reviews by Fairweather *et al.* (1952), and by Smit and Wijn (1954), and therefore will not be discussed here. Since these reviews appeared, however, a new substance of this group has provided further confirmation of Néel's theory of ferrimagnetism. He had predicted that the variation of magnetization with temperature might follow any one of eight types of curve, arising as algebraic sums of the curves for the two opposing sub-lattices in the ferrimagnetic material (although two of these types have been thought to infringe the Third Law of Thermodynamics). One of these curves passes through a zero at a 'compensation temperature' before increasing again and finally reaching zero again at the Curie temperature; Gorter (1954) produced a lithium ferrite-chromite which showed this behaviour, inexplicable except on Néel's theory.

8.1.2. *'Hexagonal'-type compounds*

Four groups of compounds having hexagonal symmetry are now known. The more complicated ones may be thought of as compounds of barium ferrite, BaFe_2O_4 (which is non-magnetic) with various proportions of other known ferrites including a divalent ion (Jonker *et al.* 1957). Some of the resulting compounds are magnetically soft. Their technical interest lies in their properties at frequencies of over 100 Mc/s, which are discussed in § 9.

8.1.3. *Garnet-type compounds*

The garnet-type compounds contain the oxide of any one of the eleven rare-earth metals from Gd to Eu inclusive (Pauthenet 1958) and are therefore expensive, difficult to obtain in pure form, and unlikely to be commercially important (with a possible exception mentioned below). Aluminium, gallium, or chromium can be substituted for some of the iron ions (Gilleo and Geller 1958). Most of them have a 'compensation temperature' at which the magnetization passes through zero.

The yttrium-iron garnet is unique in two respects. It is transparent in the infra-red and possibly in the visible region too, and might therefore allow the construction of a rapidly actuable modulator for an infra-red beam. Further, when in single-crystal form its resonance in the microwave region is the sharpest one known, the frequency being determined by the applied field, and the line-width being less than 1 Oe. (LeCraw *et al.* 1958). This makes it a promising material for the 'parametric amplifier' (Suhl 1957) which is one of the few known types of amplifier for microwave frequencies.

At the time of writing few data are available about these materials except the magnetization/temperature curves.

8.2. *Properties of Ferrites*

The importance of these materials is two-fold. In the first place they provide simple and direct confirmation of negative exchange interaction

and of indirect-exchange interaction in solids which is complementary to the direct positive exchange observed in the ferromagnetics. Secondly, they are essentially ionic compounds (but see Goodenough and Loeb 1955) and in common with all solids of this type they exhibit negligible electrical conductivity when of stoichiometric composition. Consequently eddy currents are virtually absent and they may be used with advantage at frequencies at which ordinary ferromagnetics would be useless even in thin laminations.

In their macroscopic properties, ferrites do not differ much from metallic ferromagnetics. Owing to the negative interaction between ions on different sub-lattices the net moment of ferrites is usually smaller than that of typical ferromagnetic metals and alloys. Their crystal anisotropies and magnetostriction constants are usually comparable with those of metals and since both metals and ferrites are found to possess cubic or hexagonal structures, these properties obey the same symmetry laws in both types of material. A single crystal of a ferrite thus possesses low-field magnetic characteristics which are identical in nature with those of metal crystals. In very low fields the latter are invariably 'softer' but this may be due to the more advanced technique of making pure homogeneous metal crystals.

In polycrystalline material a further complication arises owing to the porosity of the ferrites—a feature absent from polycrystalline metals. The degree of porosity† in a ferrite is a function of its method of preparation and may be as little as 3% or as high as 50%; usually it is sufficient to ensure that the d.c. resistivity is governed only by the inter-crystalline boundaries and not by the intra-crystalline material (Guillaud 1957). Although it is quite easy to see, in general terms, what the effect of porosity on magnetic properties is likely to be, it is virtually impossible to make any reliable qualitative estimates. Unless the grain size is very large (which it usually is not) closure domains probably cannot form on grain boundaries to a degree sufficient to ensure zero divergence of I_s . Consequently surface poles must be formed and internal magnetic fields will appear. Thus the field acting upon any grain (labelled k) will be the external field H_e plus the internal field $\mathbf{H}_i^{(k)}$, i.e. $\mathbf{H} = \mathbf{H}_e + \mathbf{H}_i^{(k)}$. $\mathbf{H}_i^{(k)}$ will depend upon the shape and size of the grain and also those of its neighbours and the direction of the magnetization within them. It will also be proportional to some function of the anisotropy constant since the smaller this is, the greater is the likelihood of the formation of closure domains or of rotation of the magnetization at the surface of the grain thereby reducing the pole density. These factors conspire to make a calculation of $\mathbf{H}_i^{(k)}$ exceedingly difficult. In low fields, however, $\mathbf{H}_i^{(k)}$ may be expected to be given by some distribution function centred around zero so that it may be either positive or negative with respect to the applied field. In this case the presence of the internal fields will make the material magnetically harder than it would be if they were absent since the external field now has to overcome the internal field before

† The porosity may be defined as $(\rho_x - \rho_A)/\rho_x$, ρ_x and ρ_A being the x-ray and apparent densities respectively.

it can compete with the internal barriers to magnetization processes (e.g. domain wall impedance). This effect will be most marked in those properties such as coercive force and maximum permeability which imply the surmounting of a definite critical field and experimentally it is observed that both these quantities are very sensitive to porosity (Smit and Wijn 1954). Closely related to this problem is the much debated question of the origin of the initial permeability in sintered ferrites—see § 9.3.1.

In the rest of this review, no attempt is made to treat ferrites and metallic ferromagnetics separately.

§ 9. FREQUENCY DEPENDENCE OF MAGNETIC PERMEABILITY AND RELATED TOPICS

9.1. *Types of Variation with Frequency*

Optical properties of ferromagnetic substances, and in particular the fact that they obey the well-known Hagen–Rubens relation, indicate quite clearly that their permeability is unity at infra-red frequencies. Within this frequency range of about 0 – 10^{14} c/s the variation of permeability with frequency is often complicated and varies from one substance to another. Measurements of permeability show that in ferrites it becomes unity above about 10^9 or 10^{10} c/s (Welch *et al.* 1950, Jonker *et al.* 1957).

In this connection it is convenient to regard the permeability μ as a complex quantity $\mu_1 - i\mu_2$. The loss angle ϵ is given by $\tan \epsilon = \mu_2/\mu_1$. Various methods are available for determining μ_1 and μ_2 ; for example, the in-phase and quadrature balance conditions of an a.c. bridge. It is frequently of practical importance to quote results in terms of μ_1 and $\tan \epsilon$. No additional information is conveyed but the latter quantity is a convenient measure of the power loss in the magnetic material. Thus it is logical to treat the frequency dependence of magnetic permeability and alternating-current losses together, since they are different manifestations of the same thing. Further, the quantities μ_1 and μ_2 are not independent but obey the well-known Kramers–Kronig dispersion relations. Thus measurement of μ_1 or μ_2 at two different frequencies can, in principle, be made to yield the same information as simultaneous measurement of μ_1 and μ_2 at a single frequency. For practical reasons, it is, however, often convenient to use the latter procedure.

The observed dispersion of magnetic permeability frequently results from a superposition of several mechanisms and care may be needed to separate one from another. In metals the principal mechanisms are likely to be

- (1) eddy current effects,
- (2) dimensional resonance,
- (3) relaxation and/or resonance phenomena,
- (4) effects associated with thermal activation of domain boundaries (Néel 1951, Street and Woolley 1949),
- (5) relaxation mechanisms associated with atomic diffusion (Snoek, 1938, 1939 a, b).

Dimensional resonance is the setting up of a standing wave by reflection between the opposite surfaces of a specimen; it is observable in ferrites, in which the permittivity is often large (Fairweather *et al.* 1952).

Of these, (1) and (2) differ from the others in being size-dependent. Thus it is possible in principle to reduce eddy-current effects to negligible proportions by the use of very thin sheets. Technical difficulties of fabrication conspire to prevent this being done in practice. Of the remainder, mechanisms (4) and (5) are characterized by such a long relaxation time (or distribution of long relaxation times) that they may be observed either as time-effects or low-frequency losses.

In ferrites eddy-current effects will normally be small but in addition to (4) and (5) above there is now the possibility of electronic diffusion between ions. This may give rise to the type of transition such as is observed in magnetite near 119°K at which temperature the electron-exchange between Fe^{2+} and Fe^{3+} ions becomes so slow that an ordered $\text{Fe}^{2+}\text{Fe}^{3+}$ structure can be frozen in on the B sites. Above this temperature the possibility of the electron interchange gives rise to after-effects and relaxation phenomena. In ferrites too the dielectric constant is large and many of the mechanisms responsible for magnetic relaxation effects will give rise to dielectric dispersion as well.

The dispersion of an observed quantity is usually classified into one of the two limiting cases of resonance and relaxation. Mathematically, the first arises when the system can be described by a differential equation of the form

$$m\ddot{x} + \beta\dot{x} + \alpha x = F \exp(i\omega t) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the solution of which exhibits typical resonance characteristics. The resonance may be extremely broad however if $\beta/m \gg \alpha/m$ but only in the limiting case in which $m \rightarrow 0$ does the solution pass over to the relaxation type. Between the two there is therefore a gradual and continuous transition and experimentally it may be very difficult to distinguish between the two types. Useful criteria have been given by Miles *et al.* (1957).

9.2. Eddy-current Effects

In metals, eddy-current screening accounts for the major part of the dispersion of permeability for frequencies up to about 10 Mc/s. The standard eddy-current calculations (Thompson 1892, Cauer 1925, Scott 1930) use Maxwell's equations and assume the material to be characterized by a uniform scalar permeability. In order to render the resulting equations mathematically tractable it is necessary to impose the further restriction that the permeability is independent of the magnetizing field. Thus the calculations are strictly valid for para- and diamagnetic substances only. In ferromagnetics the second restriction can usually be satisfied in practice by working with very weak fields. In consequence, the standard eddy-current equations may be used with confidence only in the initial-permeability region. This is not to say that they are totally irrelevant

to the situation at high inductions but merely that precise numerical agreement between calculation and experiment is not to be expected under these conditions.

The requirement of spatially uniform permeability, however, cannot be satisfied by suitable choice of experimental conditions and is hardly compatible with our present knowledge of ferromagnetic domains and of magnetization by moving domain boundaries. Rather, it is clear that the measured permeability of a substance must represent an overall effect, with the local permeability ranging from extremely large values to small ones depending on whether a given volume contains moving domain boundaries or not. The only issue is whether the non-uniformity of permeability seriously invalidates the calculations.

Experimentally, most of the evidence comes from measurements carried out on ultra-thin laminations. It is usually found that the permeability of such laminations decreases with frequency much more rapidly than is indicated by the usual eddy-current formulae, the discrepancies becoming more marked as the lamination thickness decreases. An equivalent observation is that the losses, which should vary as the inverse square of the lamination thickness, actually decrease much less rapidly, being greater than those calculated. This is a matter of some practical importance, since materials are laminated especially to reduce these losses, and yet the lamination process is not as effective as it should be. At one time this effect was ascribed to layers of inferior material, having a lower permeability, at the surfaces of sheets, these layers becoming proportionately more important as the material is made thinner (Peterson and Wrathall 1936). Feldtkeller (1952), however, showed that one particular model of this kind led to ratios of observed to calculated loss not exceeding 1.6; other models would presumably lead to numerical factors of the same order; yet Abgrall and Epelboin (1952) reported ratios of up to 18, in strip a few microns thick, and Richards *et al.* (1957) found values agreeing with theirs.

It now seems to be established that these effects are attributable to the effect of the non-uniform permeability which is a direct consequence of the existence of a domain structure. The effects are trivial in the sense that they arise from an attempt to account for experimental results in terms of a mathematical analysis which does not take into account the existing physical situation. In fact it seems that the assumption of a uniform permeability always results in an under-estimate of eddy-current effect.

Actual domain structures are frequently complicated and any calculation of eddy currents which takes into account the existence of moving domain walls must necessarily be based on a model which is sufficiently simple to permit reasonably exact mathematical analysis. For an infinite sheet, traversed at regular intervals by domain boundaries perpendicular to the plane of the sheet (see fig. 1), Polivanov (1952) obtained for the complex permeability

$$\frac{\mu^*}{\mu} = 1 - \frac{32i\xi(L/d)}{\pi^2} \sum_{\text{odd } n} \frac{1}{n^3 \tanh(n\pi L/d) + 4in^2\xi(L/d)} \quad . \quad . \quad (4)$$

where the symbols L and d are defined in fig. 1 and $\xi = \omega\mu d^2/\rho$ is the usual skin depth parameter with ρ equal to the resistivity. This expression fits the experimental results much more closely than does the usual one. Some idea of the difference between the two expressions may be seen by comparing them in the low-frequency limit which corresponds to the situation in which the skin depth is much greater than d . In this case the equation becomes

$$\frac{\mu^*}{\mu} = 1 - \frac{32i\omega\mu Ld}{\pi^2\rho} \sum_{\text{odd } n} n^{-3} \coth \frac{n\pi L}{d}.$$

The (angular) relaxation frequency is thus

$$\omega_{\text{domain}} = \frac{\pi^2\rho}{32\mu Ld \sum_{\text{odd}} n^{-3} \coth (n\pi L/d)}.$$

The corresponding relaxation frequency given by the uniform permeability approximation is

$$\omega_{\text{uniform } \mu} = \frac{3\rho}{\pi\mu d^2}.$$

The ratio, which is a measure of the discrepancy between the two calculations, or of the inadequacy of the uniform-permeability model, is therefore

$$\eta = \frac{\omega_{\text{uniform } \mu}}{\omega_{\text{domain}}} = \frac{96}{\pi^3} \frac{L}{d} \sum_{\text{odd}} n^{-3} \coth \frac{n\pi L}{d};$$

$\eta \rightarrow 1$ as $L/d \rightarrow 0$ and η is not significantly greater than unity for values of L/d less than 0.1. When $L/d = 1$, however, η is about 3. Thus, as long as the average distance between successive domain walls is less than about one-tenth of the lamination thickness, the effect of the domain structure is inconsiderable and the standard eddy-current calculations may be regarded as approximations, sufficiently precise for most practical purposes. When the average domain size becomes comparable with this thickness, however, the alternative eqn. (4) must be used. Exact agreement between this equation and experiment is not to be expected since in any real material there is likely to be a distribution of domain size L about some mean value.

Eddy-current losses at high inductions are of great practical importance in connection with power transformers and rotating machinery. Once again, the measured loss is invariably greater than that calculated from the standard equations, sometimes by a factor of about three; this is the so-called eddy-current anomaly. At high inductions hysteresis becomes significant and the relation between B and H may no longer be regarded as approximately linear. Moreover, under these conditions the instantaneous domain configurations cannot be ascertained so that the choice of a particular domain model for purposes of calculation is to a certain extent arbitrary and is judged almost solely from the sole criterion of explaining the observed losses. The most successful model to date is that of Aspden (1956) who assumes that the magnetization of an infinite thin sheet may be regarded

as taking place by movement of a single plane wall in the plane of the sheet. In this case the rate of eddy-current loss as the flux passes through zero is exactly three times that calculated on a uniform-permeability basis. Thus there seems to be nothing really mysterious about the eddy-current anomaly. Theoretically it is complicated by the facts mentioned above. In practice it is often sufficient to know that it exists.

9.3. Relaxation and Resonance Phenomena

9.3.1. In the range 1 to 1000 Mc/s.

At sufficiently high frequencies wall displacements may be expected to be damped out almost completely by the resulting eddy currents leaving only the rotational processes. At 200 Mc/s Johnson *et al.* (1947) found that the permeability of polycrystalline iron could be wholly ascribed to rotational processes. In ferrites, however, and at the surface of ferromagnetic conductors, eddy-current effects are absent. Nevertheless relaxation effects are observed. If domain wall inertia effects are absent, eqn. (3) becomes

$$\beta \dot{x} + \alpha x = F \exp(i\omega t).$$

For a 180° wall $F = 2HI_s$. The wall motion is viscously damped and the resulting permeability is $\mu_1 - i\mu_2$, where

$$\mu_1 = \frac{\mu_0}{1 + \omega^2 \beta^2 / \alpha^2}$$

and

$$\mu_2 = \frac{i\omega \beta / \alpha \mu_0}{1 + \omega^2 \beta^2 / \alpha^2},$$

where μ_0 is the permeability at zero frequency. Observations by Galt (1954) using a single-crystal ferrite having a simple domain structure are in agreement with these equations and thus point to an intrinsic, size-independent wall damping. The damping constant β is related to the damping term in the Landau-Lifshitz (1935) equation, viz.

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M} \times \mathbf{H}) - \frac{\lambda}{M^2} [\mathbf{M} \times (\mathbf{M} \times \mathbf{H})] \quad . \quad . \quad . \quad (5)$$

through the relation

$$\beta = \frac{2\lambda I_s^2}{(\gamma^2 I_s^2 + \lambda^2) \Delta}$$

where $\gamma (= ge/2mc)$ is the magneto-mechanical ratio and Δ is the effective width of the domain wall.

Domain wall damping of this kind must occur in ferromagnetic metals as well as ferrites. Usually it is so obscured by eddy-current damping as to escape observation. However, in very high permeability alloys the spin relaxation frequency may be quite low. As an example consider a typical alloy with $\mu = 30\,000$, $I_s = 600$ gauss, $\lambda = 2 \times 10^8 \text{ sec}^{-1}$ (this is the value for

Supermalloy, Bloembergen 1950), $\Delta = 10^{-4}$ cm. Analysis of eddy-current losses in thin sheets by Lee (1958) led to an estimated domain size of about 25×10^{-4} cm. Then since $\mu = 8\pi I_s^2 / \alpha L$, this gives $\alpha \simeq 2 \times 10^5$. In addition $\beta \simeq 10^{-2}$, so that the angular relaxation frequency is about 20 Mc/s; in materials with larger domains it might be much less. In any case it is clear that the interpretation of measurements carried out in the neighbourhood of this frequency will be seriously in error if it is assumed that the observed effects are solely due to eddy currents.

In ferrites it is frequently found that there are two dispersion regions in both of which resonance characteristics are apparent. Rado and his co-workers have advanced the suggestion (see, for example, Rado 1953) that the lower of these two resonances which are usually found in the r.f. region is due to domain wall resonance whilst the upper is due to spin resonance (Larmor resonance) in the anisotropy field. Workers at the Philips Research Laboratories are inclined to attribute both to spin resonance (Smit and Wijn 1954) and take the view that the lower resonance is associated with internal fields arising from the porosity of polycrystalline samples. The controversy remains open because it is very difficult to devise an experiment whose results *cannot* (with some ingenuity) be interpreted in either way. It has been established beyond doubt that in single crystals the initial permeability is attributable to domain boundary displacements (Galt *et al.* 1953, Galt 1954); while the high-frequency properties of the 'hexagonal' ferrites (§ 8.1.2) suggest rotations. It may well be that the first interpretation is correct for some materials and the second for others. Thus for high-density ferrites with large grain size the domain wall resonance interpretation might well be the correct one, whereas in low-density ferrites with small grain size an r.f. resonance might equally well be explained in terms of spin-resonance in the internal demagnetizing fields. The situation is complicated by the fact that the dielectric constant of most ferrites is very high. In these circumstances it is necessary to take in account the displacement as well as the conduction current. But whereas the internal magnetic field produced by the latter is always (by Lenz's Law) such as to oppose the applied field, that due to the displacement current is in phase with it. This should give rise to quasi-resonance effects (Polivanov 1952) but on account of the low Q of the system the resonance will not be very sharp.

9.3.2. In the microwave range

Resonances in the micro-wave region are definitely attributable to spin-resonance in the anisotropy field of the sample as predicted by Landau and Lifshitz (1935). For a random polycrystal and in an approximation in which domain interactions are ignored Kittel (1951) derived the following expression for the rotational susceptibility

$$\frac{\chi(\omega)}{\chi(0)} = \frac{\omega_0^2 + (\lambda/\chi') [i\omega + (\lambda/\chi')]}{\omega_0^2 + [i\omega + (\lambda/\chi')]^2} \quad \dots \quad (6)$$

in which χ' is an average rotational susceptibility approximately equal to $\chi(0)$. In this expression ω_0 is the resonance frequency in the anisotropy field. Thus

$$\omega_0 = \gamma H_{\text{anis.}}$$

with

$$H_{\text{anis.}} = \frac{2|K|}{I_s} \quad (17)$$

and

$$\gamma = ge/2mc.$$

In a polycrystalline material the anisotropy field may be modified by local stresses and inhomogeneities so that there is a distribution of values of the internal field about $H_{\text{anis.}}$, giving rise to severe broadening of the resonance spectrum.

The connection between domain wall resonance and spin resonance now becomes clear if it is remembered that the motion of the spins in a moving domain wall is a rotation similar to that envisaged as taking place in the spin resonance. But, as pointed out by Roberts (1953 b) the internal field acting on a domain wall is of the order of the coercive field which is usually very much less than the anisotropy field given by eqn. (7) and the resonance frequency is correspondingly lower.

In either case the resonance is damped but the exact nature of the damping mechanism remains unknown. Equation (6) is derived from the equation of Landau and Lifshitz (1935) eqn. (5) in which the damping constant λ is introduced formally without regard to its origin or to the mechanism responsible for its appearance. Even the form of this equation has been criticized by Gilbert (1955) who pointed out that for very large λ the damping torque is bigger than the applied torque and so \mathbf{M} does not move in the direction of the applied torque, $\mathbf{M} \times \mathbf{H}$. This is clearly an impossible result and Gilbert (1955) proposed a modification of eqn. (5), namely

$$\frac{d\mathbf{M}}{dt} = \gamma(\mathbf{M} \times \mathbf{H}) - \frac{\lambda'}{M^2} \left\{ \mathbf{M} \times \frac{d\mathbf{M}}{dt} \right\} \quad (8)$$

which reverts to the form of the Landau-Lifshitz equation for small values of the damping constant. No further light is shed on the mechanism of the damping process by this modification, however, and even its origin is obscure. The present theoretical situation is well reviewed by Kittel and Abrahams (1953) and by Abrahams (1954).

If a static magnetic field is applied this field is added to the anisotropy field and the resonance frequency is shifted to a higher value. The general character of the resonance remains unchanged, however, and the width of the absorption line may be used to obtain information concerning the magnitude of spin damping. Whether, however, the ferromagnetic resonance experiments give the same value for λ (or λ') as is found from the wall relaxation experiments (which are carried out at a much lower frequency) is not too clear. The measurements of Galt (1954) on magnetite and nickel-iron ferrite indicate that differences exist between the values obtained by the two methods which point to a frequency variation of λ .

The difficulty lies in the measurement of λ at low frequencies, particularly in metals since it is necessary to find some means of eliminating eddy-current damping. A start in this direction has been made by Kelly (1956), who measured the rotational damping by observing the rate of retardation of a thin disc, spinning rapidly in a strong magnetic field. The results give clear indications of a size-independent damping but no quantitative conclusions have yet been drawn.

9.3.3. *Internal spin resonance in hexagonal ferrites*

The interpretation of the dispersion of the initial permeability in ferrites in terms of rotational resonance in the anisotropy field has been used to develop new ferrites for use at ultra-high frequencies. The resonance frequency is related to the internal field by the usual expression $\omega = \gamma H_{\text{int}}$. The anisotropy field is distributed about a mean value by crystal imperfections, grain boundaries, etc. and the resonance frequencies are similarly distributed in consequence, and in the case of dispersion by resonance no magnetic material can have a permeability significantly greater than unity above the highest resonance frequency unless the resonance is heavily damped (in which case the losses will be large). Therefore a material which is to be usable up to very high frequencies must have a high natural resonance frequency. This can be achieved by a high internal field. Since the internal field is related to the anisotropy constant K by the relation

$$H_{\text{int}} = \frac{2|K|}{I_s}$$

which holds for cubic materials only, and since in this case the rotational susceptibility is

$$\chi_{\text{Rot}} = \frac{I_s^2}{3K}$$

it follows that there is an inverse relationship between H_{int} and χ_{Rot} . Consequently the maximum usable frequency is roughly

$$\omega_{\text{max}} = \gamma H_{\text{int}} = \frac{2I_s}{3\chi_{\text{Rot}}}$$

so that a high usable frequency can be obtained in cubic materials only by the use of low permeability material.

In the new hexagonal ferrite (Jonker 1956, Jonker *et al.* 1957) the anisotropy is low in the basal plane and consequently χ_{Rot} is high although the magnetization vectors are confined to this plane. On the other hand the resonance frequency is determined not only by the equivalent internal field in the basal plane but also by that at right angles to it. Denoting these two anisotropies by K_{\parallel} and K_{\perp} respectively the rotational susceptibility is now

$$\chi_{\text{Rot}} = \frac{I_s^2}{3K_{\parallel}}$$

but the resonance frequency is

$$\omega = \gamma(H_{\parallel}H_{\perp})^{1/2} = \gamma\left(\frac{2}{3}\right)^{1/2}K_{\perp}^{1/2}\chi_{\text{Rot}}^{-1/2} \quad \dots \quad (9)$$

for a hexagonal material. Equation (9) is similar to the expression used to interpret ferromagnetic resonance experiments in which the demagnetizing field at right angles to the specimen plays an important part in determining the resonance frequency. In general $K_{\perp} > K_{\parallel}$ so such a material has a permeability significantly greater than unity which is retained up to frequencies approaching 10^3 Mc/s. The permeabilities found are usually of the order 10, which is small by ordinary standards, but is an improvement on those of other materials which differ little from unity at these frequencies.

9.4. Switching Time

Closely allied to the frequency dispersion of magnetic permeability is the problem of the time taken for a ferromagnetic material to reverse its magnetization. This question is now of considerable practical importance in connection with the use of small magnetic cores as memory devices in computers. The switching time T is related to the driving field H by the relation

$$1/T = S(H - H_0)$$

where S is a constant, characteristic of the material, and H_0 is equal to the coercive field in ferrites but is somewhat greater in metals.

In thick metallic materials the constant S depends on the eddy currents set up, and is calculable from the thickness and resistivity. In thin materials the constant is smaller than the one so calculated, and becomes independent of thickness (Menyuk and Goodenough 1955). Here 'thick' and 'thin' are relative to the domain size, which may be of the order of 10 microns in normal materials but may be much larger in those having markedly rectangular hysteresis loops; the latter therefore switch very slowly and are in fact not usable in computers. In ferrites the constant S is, approximately at least, inversely proportional to the coercivity; SH_c is about 10^6 sec^{-1} . For materials suitable for use in computers, S is of the same order in metals and ferrites; it is not known whether this is merely accidental.

This limit to the rapidity of reversals implies a dip in the permeability/frequency curve at frequencies of the order of 1 Mc/s. In metals this is difficult to observe, because in material of any ordinary thickness it is masked by the effects of eddy-current screening. It might be due either to spin-relaxation or to localized eddy current (§ 9.2). In ferrites the effect is known, and Polder (1950) showed the relaxation frequency to be proportional to $1/\mu$ —which implies that it is roughly proportional to H_c .

The response of a magnetic material to a sharply changing field often appears to consist of two superposed processes. The slower, and usually the major part of the response, is the result of domain-wall movement, and has the time-constant already discussed. A faster process, having a time-constant of the order of tens of millimicroseconds, is probably rotational. In conventional materials it is not important, but in thin films it can be made to predominate. The evidence for this is given in § 4.4.

9.5. *Jordan Effect*

Jordan (1924) drew attention to an energy loss in magnetic materials at low flux densities which (like hysteresis loss) is proportional to frequency over a wide range, yet (unlike it) proportional to the square of the flux density†. It varies little with temperature. It is the loss described by Néel (1951) and Barbier (1951) under the name 'trainage irréversible' (implying that the process is thermodynamically irreversible) and ascribed by them to random activation of domain walls by thermal agitation. Such a process, if it occurs at all, must occur in all ferromagnetic materials.

Feldtkeller (1953 b) distinguished a second loss, similar to Jordan effect, but observable in a restricted range of frequencies of the order of 100 kc/s. It may be due to thermal conduction, dissipating the energy liberated in the regions swept by domain walls.

9.6. *Richter Effect*

Richter (1938) showed that there is another type of loss which varies with frequency and with flux density in the same way as that due to Jordan effect, but which is strongly dependent on temperature, its time-constant varying a hundredfold between 17 and 90°C. The proportionality to frequency holds only within a limited range of frequencies (perhaps 100 : 1). Richter's own observations were made by ballistic methods, but were confirmed by Schulze (1938) using a.c. methods. The effect can probably be identified with Néel's 'trainage réversible' observed in d.c. tests.

Richter and Schulze found the effect in well-annealed 'carbonyl iron' (i.e. iron made by powder metallurgy from carbonyl iron powder), but not in cold-worked material. (This contrasts with Bozorth's remark (1951, p. 796) that residual loss tends to be higher in cold-worked substances—but he was referring to Jordan, not Richter, effect.) Snoek (1939 a), again using carbonyl iron, found abnormally high Richter effect when carbon or nitrogen were introduced during heat treatment. Rathenau (1958), using d.c. methods at temperatures low enough to produce conveniently long time-constants, has distinguished five components of Richter effect in nearly pure iron, one associated with carbon impurity, three with nitrogen, and one of unknown origin. Because of experiments of this type, Richter effect is ascribed to the migration of foreign atoms through the crystal lattice under anisotropy forces, a process which requires finite time and therefore appears as a loss in a.c. conditions. The strong dependence on temperature is consistent with this explanation.

Feldtkeller and his co-workers (Feldtkeller 1953 a, b, Sorger 1953) have shown a similar effect to exist also in ordinary silicon-iron; this might well contain both carbon and nitrogen, depending on its heat-treatment during manufacture.

† On grounds of network theory, Feldtkeller points out that this relation can hold only in a restricted range of frequency. His objection assumes that it must be possible to represent the material by a *finite* network (Roberts 1953 a).

Dunton (1953) reported an effect, similar to Richter effect but hundreds of times slower, in cores made from insulated particles of carbonyl iron. As this iron is certainly distorted in pressing into cores the effect can hardly be the same as Richter's.

Feldtkeller (1953 a, b) mentions other anomalies which are found accompanying the Richter effect: e.g. the observed a.c. loss is not that which would be calculated from the change of permeability with field, assuming the Rayleigh loop to apply. Another anomaly (Feldtkeller 1952) observable with a.c. is a slow change, continuing for several hours, in the shape of the hysteresis loop. (This is Néels' 'reptation'; see Néel 1959.)

The names 'residual loss', 'after-effect', and 'magnetic viscosity' are used interchangeably to cover the Jordan and Richter effects taken together.

9.7. Losses in Carbonyl Iron Powder

An unsolved puzzle is the extraordinarily low a.c. loss found in some types of carbonyl iron powder. This material consists of roughly spherical particles, of diameter of the order of 5 microns; it is made by the decomposition of the vapour of iron carbonyl, and it may or may not be subjected to a decarburizing and annealing process before use. For technical use an insulating material is applied so that every individual particle is thinly coated, and it is then pressed into a solid block of the required shape. Practically all the reported data are for material which has been pressed in this way.

The observed eddy-current loss can be compared with that calculated for an array of spheres of the appropriate resistivity. The hysteresis and residual losses are not predictable in any such way, but comparison with those of other materials shows that they are small. The low losses of unannealed material (Richards 1953), whose composition and mechanical hardness are those of a nitrided steel, are quite unexpected. The only further evidence available is some x-ray work showing that the pressed material is severely strained, and photographs of etched sections which show an onion-like structure in E-type particles (Taylor 1953). These photographs suggest the presence of spherical shells of two different phases, occupying roughly similar total volumes, but it is difficult to suggest what they might consist of.

For most applications these materials are being gradually superseded by ferrites, and this problem is therefore likely to be left unsolved.

ACKNOWLEDGMENTS

We would like to express our thanks to all those who, in one way or another, have contributed towards this review: Professor L. F. Bates who has constantly kept us in touch with new developments; authors, too numerous to name individually, who have kindly sent reprints of their published work; and the writers' colleagues for advice and discussions.

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